

TECHNOLOGY DEPARTMENT

EXHAUSTIVE TRACE IMPURITY ANALYSIS OF NIOBIUM
MATERIALS MADE BY THREE DIFFERENT PROCESSES

(Kemet P.O. No. 233-43144)

Contract NObsr-87478 Bureau of Ships
Department of the Navy

By

A. R. Gahler

Job Order No.
840-95379-P

June 7, 1963

METALS RESEARCH LABORATORIES
TECHNICAL REPORT NO. P-63-11

SECURITY COPY

UNION CARBIDE METALS COMPANY
DIVISION OF UNION CARBIDE CORPORATION

4625 ROYAL AVENUE, P. O. BOX 580
NIAGARA FALLS, NEW YORK

EXECUTIVE OFFICES 270 PARK AVENUE NEW YORK 17, N. Y.

UCCNHT0000219

EXHAUSTIVE TRACE IMPURITY ANALYSIS OF NIOBIUM
MATERIALS MADE BY THREE DIFFERENT PROCESSES

BY

A. R. GAHLER

Kemet P. O. No. 233-43144

Contract NObsr-87478
for
Bureau of Ships
Department of the Navy
Washington, D. C.

June 7, 1963

UNION CARBIDE METALS COMPANY
Union Carbide Corporation
Technology Department
Niagara Falls, New York

UCCNHT0000220

TABLE OF CONTENTS

	<u>Page</u>
<u>ABSTRACT</u>	
<u>LIST OF TABLES</u>	
I. <u>INTRODUCTION</u>	1
II. <u>PREPARATION OF METAL POWDERS</u>	2
III. <u>COMPOSITION OF METAL POWDERS</u>	3
IV. <u>ANALYTICAL METHOD DEVELOPMENT</u>	5
A. Experimental	7
1. Separations	7
a. Liquid-Liquid Extractions	7
b. Liquid Anion Exchange	7
c. Column Anion Exchange	7
2. Analytical Methods	8
a. Spectrophotometric Methods	8
(1) Zirconium	8
(2) Tin	8
(3) Titanium	9
(4) Vanadium	9
b. Emission Spectrographic Methods	10
(1) Aluminum	10
(2) Silicon	10
(3) Zirconium, Titanium, Vanadium, Tin	11
(4) Lithium	12
V. <u>SUMMARY OF ANALYTICAL METHODS</u>	12
VI. <u>CONCLUSIONS</u>	16
VII. <u>REFERENCES</u>	17
VIII. <u>CONTRIBUTING PERSONNEL</u>	18

	<u>Page</u>
<u>APPENDIX I</u> - Spectrophotometric Methods for Trace Elements in Niobium Metal	
1. Chromium	I-1
2. Cobalt	I-4
3. Copper and Nickel	I-7
4. Iron	I-10
5. Manganese	I-13
6. Molybdenum	I-15
7. Tantalum (without ion exchange separation)	I-17
8. Tantalum (after ion exchange separation)	I-20
9. Tin	I-23
10. Tungsten	I-25
11. Zirconium and Titanium	I-27
<u>APPENDIX II</u> - Emission Spectrographic Methods for Trace Elements in Niobium Metal	
1. Aluminum	II-1
2. Boron	II-4
3. Calcium and Magnesium	II-7
4. Aluminum, Lithium, Silicon, Tin, Titanium, Zirconium (Direct Method)	II-9
5. Zirconium, Titanium, Tin, and Vanadium (After ion exchange separation)	II-13
<u>APPENDIX III</u> - Miscellaneous Analytical Methods	
1. Carbon	III-1
2. Nitrogen (Distillation - Titrimetric Method)	III-3
3. Nitrogen (Distillation - Spectrophotometric Method)	III-5
4. Oxygen and Hydrogen	III-8

EXHAUSTIVE TRACE IMPURITY ANALYSIS OF NIOBIUM
MATERIALS MADE BY THREE DIFFERENT PROCESSES

ABSTRACT

Three lots of niobium metal by different manufacturing processes were reduced to powder, analyzed, and submitted to Kemet for evaluation for use in capacitors.

New analytical methods for the determination of less than 20 p.p.m. of titanium, aluminum, silicon, vanadium, tin, and zirconium in niobium were developed. These new methods were necessary in order to know precisely the compositions of the types of niobium tested in this contract.

LIST OF TABLES

	<u>Page</u>
TABLE I - Oxidation Effect of Exposure of Niobium Powder to Air	2
TABLE II - Comparison of Hydrogen, Oxygen and Nitrogen Content of Niobium Metal Before and After Hydriding	3
TABLE III - Analyses of Niobium From Three Different Processes	4
TABLE IV - Other Elements Sought but Not Detected In Any of the Niobium Materials	5
TABLE V - Method and Lower Limit of Detectability for Analysis of Trace Elements in Niobium Metal	12

EXHAUSTIVE TRACE IMPURITY ANALYSIS OF NIOBIUM
MATERIALS MADE BY THREE DIFFERENT PROCESSES

I. INTRODUCTION

In the latter part of 1962 a contract between Kemet Department, Linde Company, and the Navy was initiated to study and develop niobium capacitors. A subcontract to Union Carbide Metals Company, Metals Research Laboratory, was awarded to assist in extensive chemical analysis work and method development. It was anticipated that a co-ordinated electrical and composition evaluation of the niobium metal used for preparation of capacitors would help identify the impurities mainly responsible for degradation of dielectric niobium oxide films.

Three lots (50 pounds each) of niobium from three different manufacturing processes were received from Kemet:

Material 1 - Niobium granules prepared by hydrogen-reduction of pentachlorides.

Material 2 - Niobium granules (100 mesh by down) made by carbothermic reduction of the pentoxide.

Material 3 - Niobium sheet prepared by a proprietary process.

All three lots of niobium metal were sampled and analyzed for impurities in the as-received condition. Since Material 3 was in sheet form, the metal was sampled for the oxygen determination by shearing long strips and then small pieces from these strips. Drillings throughout the plates were collected for the other determinations.

Following the initial analyses, a sizable portion of each material was returned to Kemet for the capacitor investigations. Since a particle size of less than 100 mesh was requested, it was necessary to hydride all these metals before size reduction by crushing and ball milling. The final metal powders were reanalyzed to determine impurity pickup before delivery to Kemet for evaluation for capacitors.

Several impurity elements were believed to have appreciable effect on the final capacitor and many of these elements were present in concentrations below 20 p.p.m. Thus, it was necessary to develop analytical methods of adequate sensitivity and reproducibility for the analysis. No published methods, for example, are available for titanium, zirconium, vanadium, silicon, or aluminum, as well as several other elements in the concentration range below 10 p.p.m. in niobium metal. A survey of 32 laboratories in 1961 by the Materials Advisory Board of the National Academy of Sciences, Refractory Metals Sheet Rolling Panel, indicated that analytical laboratories do not ordinarily determine trace elements below 50 p.p.m. in niobium.

This report describes the method of preparing the sample powders, composition of the powders, the analytical method development, and the analytical procedures used for the determinations.

II. PREPARATION OF METAL POWDERS

Kemet desired to study impurity effects on capacitors prepared from niobium powder (100 M x D); therefore, it was necessary to reduce the particle size of the three lots of metal.

A preliminary study of oxidation of powdered niobium metal in air was made before reducing large quantities of metal. Niobium metal (Material 2) was crushed to approximately 8 M x D in air. A portion of this material was analyzed for oxygen, the remaining material ground by hand in a dry box to 200 M x D and 325 M x D in a dry argon atmosphere. The two fractions were then analyzed for oxygen before exposure to air, then exposed to air for various periods of time and analyzed for oxygen. From the results shown in Table I, it can be inferred that no detectable increase in oxygen occurs upon exposure to air for 96 hours of 200 M x D niobium powder. A possible slight pickup of oxygen occurs with the 325 M x D powder.

TABLE I
OXIDATION EFFECT OF EXPOSURE OF NIOBIUM POWDER TO AIR*

<u>Screen Size</u>	<u>Oxygen Content (%)</u>
8 M x D (as-received)	0.30
200 M x D	
Before exposure	0.32
1 hr.	0.35
3 hr.	0.30
16 hr.	0.30
96 hr.	0.32
325 M x D	
Before exposure	0.29
1 hr.	0.34
3 hr.	0.34
16 hr.	0.34

*Reported values by the vacuum fusion method used are not more precise than $\pm 0.02\%$ at the 0.3% level.

It has been claimed by members of the ASTM Task Force for the determination of oxygen in niobium since this test was made that the powder slowly oxidizes upon long standing.

This was tested by reanalyzing a sample of powder after it had been stored in a sample bottle for six months. The oxygen, which was originally reported at 0.15%, was found to be 0.19%. Thus, the powder does gain slightly in oxygen content when stored in the presence of air.

Niobium metal is not readily crushed in the usual type of jaw crushers or reduced to powder in a ball mill but the hydrided metal can be reduced in size fairly readily. The metal was hydrogenated by Union Carbide Stellite Company at 1472°F. in hydrogen, then cooled slowly at 50° per hour, maintaining a slight positive pressure of hydrogen. Very little oxygen was introduced by the hydriding step as shown in Table II.

TABLE II
COMPARISON OF HYDROGEN, OXYGEN, AND NITROGEN CONTENT
OF NIOBIUM METAL BEFORE AND AFTER HYDRIDING

<u>Identification</u>	<u>Before Hydriding</u>			<u>After Hydriding</u>		
	<u>%</u> <u>Oxygen</u>	<u>%</u> <u>Hydrogen</u>	<u>%</u> <u>Nitrogen</u>	<u>%</u> <u>Oxygen</u>	<u>%</u> <u>Hydrogen</u>	<u>%</u> <u>Nitrogen</u>
Material 1	<0.01	0.007	0.0003	<0.01	0.64	<0.01
2	0.28	0.062	0.012	0.30	0.86	0.01
3	0.07	0.0012	0.0025	0.06	0.68	0.03

Small samples of the hydrided metal were then ball-milled in a mill lined with niobium and equipped with niobium grinding media. Materials 2 and 3 reduced in size fairly readily but Material 1, which consisted of round granules (beads) could not be reduced in size by ball milling. These granules were cold worked by rolling them to tiny platelets. It then was possible to reach the 0.9% hydrogen level. The high-hydrogen metal could be ball milled.

The process of rolling Material 1, however, introduced large concentrations of impurities. All the powdered samples were put through a Frantz Isodynamic Separator to remove tramp iron or other magnetic impurities. The Material 1 powder also was leached with hydrochloric acid to dissolve impurities but not all of the impurities were completely removed by this treatment. Because of this higher level of impurity, granules finally were sent to Kemet for size reduction in their equipment. Analysis of this material is shown in Table III. Approximately 5 pounds of each material were prepared (100 M x D), sampled for analysis, and forwarded to Kemet for evaluation.

III. COMPOSITION OF METAL POWDERS

The three lots of niobium were sampled for analysis in the as-received state. A qualitative analysis by emission spectroscopy indicated the presence or absence of various elements and the relative concentrations of those present.

Those elements known to be present were then determined quantitatively by appropriate analytical techniques. However, the analysis on the as-received metals was merely used as an indication of the concentration level of the various impurities so that it could be determined what analytical method modification or development was required. The results on the as-received metal samples are shown in Table III as well as the analysis of the final powders after hydriding and size reduction as they were submitted to Kemet.

TABLE III

ANALYSES OF NIOBIUM FROM THREE DIFFERENT PROCESSES

MATERIAL:	1 Hydrogen Reduced From Pentachloride		2 Carbon Reduced From Pentoxide		3 Proprietary Process		Method of Determina- tion
	As Recd.	H + M 100 M x D*	As Recd.	H + M 100 M x D*	As Recd.	H + M 100 M x D*	
CONDITION:							
ELEMENT, ppm							
C	30	80	70	110	80	225	(1)
O	60	1300	2800	2700	650	1500	(2)
H	71	7500	620	7800	12	6600	(2)
N	3	170	120	237	25	43	(3)
B	0.4	0.5	0.4	0.2	0.5	0.3	(4)
Al	<40 ^a	24	<40	<30	<40 ^a	30	(4)
Ca	<20	<30	20	<30	<20	<30	(4)
Cr	13	19	15	12	11	11	(5)
Co	<10	<2	<10	<2	<10	2	(5)
Cu	6	6.5	6	7	47	44	(5)
Fe	130	278	180 ^b	67	110	187	(5)
Li	--	<1	--	<1	--	5	(4)
Mg	<20	<30	<20	<30	<20	<30	(4)
Mn	<5	18	<5	<5	<5	<5	(5)
Mo	4	6.5	34	36	4	4	(5)
Ni	15	15	8	14	21	22	(5)
Si	<50	20	<50	17	<50	140	(4)
Ta	730	7800	970	1100	320	3500	(5)
						3200	(9)
Ti	<20 ^a	--	25	--	<20 ^a	--	(4)
	--	5	--	45	--	9	(7)
V	--	0.5	--	4	--	<0.5	(7)
W	58	176	400	361	<5	<5	(5)
Zr	3	--	0.8	--	1	--	(6)
	--	4	--	10	--	10	(7)
	--	4	--	9	--	15	(8)
Sn	10	--	<5	4	15	--	(5)
	--	10	--	4	--	8	(7)

NOTES: H = Hydrided

M = Milled

a = not detected

b = Average of 4 analyses ranging from 90 to 300 ppm, indicating tramp iron.

Magnetic separation was made on the final powder.

* Nominal size.

Detection Methods: (1) Combustion conductometric; (2) Vacuum fusion;
 (3) Distillation-spectrophotometric; (4) Emission spectrographic;
 (5) Spectrophotometric; (6) Extraction-emission spectrographic;
 (7) Ion exchange-emission spectrographic; (8) Ion exchange-
 spectrophotometric; (9) X-ray fluorescence.

All the final powders contained higher concentrations of carbon, nitrogen, tantalum, and, of course, hydrogen intentionally from the hydriding processes. Oxygen increased in Materials 1 and 3; chromium, manganese, tungsten increased significantly in Material 1.

The iron content of Material 2 was considerably reduced by the Frantz Isodynamic Separator since it was known that the material had been reduced to 10 M x D in iron crushers. Materials 1 and 3 increased in iron content.

Apparent discrepancies in aluminum, calcium, silicon, titanium, and zirconium result because the original analysis was made with less sensitive methods than the improved analytical methods developed for analysis of the final powder.

Several elements were not detected. These are shown in Table IV along with the estimated detection sensitivity.

TABLE IV

OTHER ELEMENTS SOUGHT BUT NOT DETECTED IN ANY OF THE NIOBIUM MATERIALS

<u>Element</u>	<u>Estimated Detection Sensitivity ppm</u>
Sb	20
Be	10
Bi	20
Cd	10
Ce	500
Cs	10
Ga	3
Ge	5
Au	10
In	5
Pt	50
K	2
Pb	5
Os	50
Pd	10
Zn	100

IV. ANALYTICAL METHOD DEVELOPMENT

Very few analytical methods for the determination of traces of various elements in niobium metal in the concentration range interested (below 20 p.p.m.) have been published. Most published papers refer to procedures applicable for quantitatively determining elements in niobium down to approximately 0.01% (100 p.p.m.) Division R, A.S.T.M., task force on chemical analysis of niobium metal has not been concerned with ultra high-purity niobium although this task force has

studied oxygen, hydrogen, nitrogen, carbon, iron, molybdenum, tungsten, zirconium, and tantalum in niobium. Most impurity specifications for niobium metal are above 100 p.p.m.; therefore, the A.S.T.M. has not evaluated techniques for concentrations below 100 p.p.m.

The Technology Analytical Laboratory has had considerable experience for the past ten years in the determination of trace elements in niobium metal; therefore, most of the elements of interest could be analyzed by established company techniques.

From the analysis of the three lots of niobium as-received metal, it was concluded that the impurity levels of the elements were such that they fell into three categories: (1) existing UCM methods which were of suitable accuracy, precision and sensitivity--tantalum, tungsten, molybdenum, carbon, oxygen, hydrogen, nitrogen, boron, chromium, nickel, iron, and manganese; (2) existing UCM methods which were applicable with minor modifications such as change in sample size or modifications in the measurement of the colored system--cobalt, copper; (3) method development would be required to adequately measure the element at low levels of concentration (<50 p.p.m.)--titanium, zirconium, vanadium, tin, and lithium. Other elements such as calcium and magnesium were not considered of sufficient importance to require better analytical methods. Aluminum and silicon were felt to be of importance and method development was carried out on these two elements and will be described in the report for Task A, Activity 6, "Preparation of Highly Purified Niobium Powders."

Since it was quite evident that it would be impossible in most cases to determine titanium, zirconium, tin, or vanadium directly in niobium metal by emission spectroscopy, X-ray spectroscopy, and spectrophotometry without a preliminary chemical separation, several separation-concentration techniques were evaluated. The separations evaluated were patterned after some of those described in the literature which involved removal of the niobium by either liquid-liquid extraction (14), liquid ion exchange (5), or column ion exchange (9, 10, 12). The desired constituent could then be determined either with a spectrophotometer or emission spectrograph. Since multiple determinations on a sample can be made simultaneously with the emission spectrograph, it would be most desirable to develop this technique. Because of the increased sensitivity of many color-forming organic reagents and better specificity, it was concluded that spectrophotometric methods should also be investigated to substantiate the emission spectrographic methods. It was found, much beyond original expectations, that some spectrophotometric methods were equivalent and even slightly more sensitive than the emission spectrographic methods.

Although it is our customary practice to study recommended methods statistically for precision, this was not possible because of the cost and time required for a program of this nature.

A. Experimental

1. Separations

a. Liquid-Liquid Extraction

Since liquid-liquid extraction is rapid, this technique was examined first. The separation of niobium and tantalum into hexone from other elements such as zirconium has been described by Milner and Edwards (14).

Unfortunately varying amounts of niobium remained in the aqueous solution after extraction which interfered with the subsequent emission spectrographic or spectrophotometric determinations.

Essentially all the zirconium remained in the aqueous phase. A hexone extraction from 25 ml. of solution containing 8 ml. of H_2SO_4 and 10 ml. of HF gave recovery values of 95.4% for a sample to which 100 micrograms of inactive zirconium were added and 96.1% for a sample containing no added zirconium.

b. Liquid Anion Exchange

This relatively new technique (5) was also tested with radioisotope zirconium-95. Zirconium from 400 ml. of H_2SO_4 (4:96) was extracted with three 25-ml. portions of chloroform containing liquid anion exchange resins LA-1 and LA-2. About 10% of the zirconium-95 remained in the aqueous phase. Back-extraction of zirconium-95 from the chloroform solution containing the liquid anion exchangers with HCl (1:3) was quantitative.

From this data it was concluded that the recovery of zirconium would always be slightly low.

c. Column Anion Exchange

Separation of niobium and tantalum from zirconium, titanium, vanadium, iron, and many other elements by column ion exchange has been demonstrated in the literature (9, 10, 12) and has been commonly used in the Technology Analytical Laboratory. Several proposed A S T.M. methods, such as determination of tantalum in niobium and tantalum, niobium, and titanium in ferrocolumbium, are based upon ion exchange separations. Thus, this method was tested for reliability in the separation of traces of zirconium, titanium, vanadium, and tin from large concentrations of niobium.

The elution characteristics of a column 8 x 3/4-inch containing Dowex 1-X10 were tested with radioisotope zirconium-95. A sample containing the isotope in a HCl (1:3) - HF (1:4) solution placed on the column and then eluted with 150 ml. of the pure acid solution of the same concentration yielded 98.4% zirconium recovery. If the sample (and zirconium) was added to the column in a solution of slightly different acid concentrations $\sqrt{HCl (1:1)-HF (1:9)}$ and eluted with 150 ml. of the same acid solution, only 87.2% of the zirconium was recovered.

The coprecipitation of zirconium-95 as cupferrate with high purity tantalum after ion exchange separation from niobium was found to give greater than 98% recoveries. Thus, ion exchange combined with precipitation in the presence of a carrier (tantalum cupferrate) is quantitative and was used as basis for the analytical

procedure for the emission spectrographic determination. Occasionally, some niobium appeared in the eluate and, of course, would interfere with the determinations. This difficulty was attributed to traces of nitric acid remaining in the eluant containing the sample which apparently changed the adsorptive qualities of the column. The procedure was written so that traces of nitric acid are removed before the sample is passed through the column.

Since no standards were available to test the analytical method, a known amount (5 micrograms) of zirconium was added to a sample of niobium which had previously been reported to contain 1.9 p.p.m. of zirconium. By the spectrophotometric procedure 6.6 micrograms of zirconium or 95.7% recovery was obtained.

The radioactive zirconium used in these studies was carrier-free and was obtained from the Oak Ridge National Laboratories. It was separated from its decay daughter, niobium-95, by a thenoyl-trifluoroacetone extraction according to the method of F. L. Moore (15) and was used within two days of the separation, making decay corrections unnecessary.

2. Analytical Methods

The methods for tin, titanium, vanadium, and zirconium were developed for Task A, Activity 1, and aluminum and silicon for Task A, Activity 6 (Preparation of High-Purity Niobium Metal). The methods for aluminum and silicon, although developed primarily for another activity, are included in this report in order to keep all methods in one collection. Details of all the analytical methods for analysis of the niobium metal are found in Appendix I, II, and III.

a. Spectrophotometric Methods

(1) Zirconium

A colored system was needed which would have the required sensitivity for measurement of microgram quantities of zirconium and also be fairly specific. Several systems had been applied at the Technology Analytical Laboratory prior to this project. Chloranilic acid (8) and pyrocatechol violet (4) suffer from lack of sensitivity. Phenylfluorone (25) is sufficiently sensitive but not particularly specific. SPADNS, a new reagent for zirconium, is not sufficiently sensitive. Phenylfluorone was finally selected as the best reagent because of its sensitivity. Interfering elements would be removed by the preliminary ion-exchange separation.

The spectrophotometric procedure, as described in the Appendix I, was tested by adding 5 micrograms of zirconium to a sample of niobium metal assumed to contain 1.9 micrograms of zirconium by emission spectrographic analysis. A recovery of 104% of the 5 micrograms added resulted.

This method was frequently used when samples were analyzed for only zirconium because of its good sensitivity.

(2) Tin

A method for tin was not considered of great importance, but a method was developed based upon UCM experience in this type of analysis.

Several reagents have been proposed and applied for tin in steels and alloys. Among those most likely to be applicable are dithiol (16, 17), phenylfluorone (13), and pyrocatechol violet (21, 22). In our experience, the pyrocatechol violet color system is very useful because a time-consuming distillation is not required. The tin is separated from the niobium by a liquid-liquid extraction which is quite rapid.

The proposed procedure which appears in Appendix I was tested by addition of 10 micrograms of tin to a one-gram sample of niobium assumed to contain <0.0005% tin by the emission spectrographic procedure (4.2 p.p.m. by the spectrophotometric method). About 95% recovery of the tin occurred.

(3) Titanium

The Union Carbide Metals Company method (Method No. 41, 73-22-157) involving reaction of titanium with sulfosalicylic acid to form a colored system which can be measured spectrophotometrically is of insufficient sensitivity for determination of titanium below 100 p.p.m. Other colorimetric methods, such as the familiar reaction of titanium with hydrogen peroxide or Tiron (24), are insensitive or non-specific.

It was decided that a preliminary separation of niobium was necessary and this was accomplished by an ion-exchange technique. Titanium was then extracted as the thiocyanate complex by tri-n-octyl-phosphine oxide (TOPO) dissolved in cyclohexane. (For complete method see Appendix I). By this technique less than 1 p.p.m. of titanium can be readily determined in niobium metal.

Since no standards are available, results from the spectrophotometric method were compared with those from the emission spectrographic procedure. On one sample of niobium metal, the average of two results by the spectrophotometric method was 10 p.p.m. (11 and 9.5 p.p.m.) whereas titanium by the emission spectrograph method was 7 p.p.m.

A new method for the determination of titanium in the presence of niobium has been proposed (19) using diantipyrylmethane. The reagent was obtained and a preliminary evaluation made of its usefulness for analysis of titanium in niobium. Although this method is quite sensitive, it would be difficult to determine less than about 5 p.p.m. titanium in niobium directly. Niobium up to 0.25 g. enhances the color slightly, but larger concentrations effect the colored system appreciably. This colored reagent could be used instead of the thiocyanate-TOPO in cyclohexane system after ion exchange separation of the niobium. Efforts to extract the titanium-diantipyrylmethane system with organic solvents were not successful. Insufficient time was available for a complete evaluation of this very interesting system.

(4) Vanadium

The reaction of N-phenylbenzohydroxamic acid with vanadium (V) has been extremely useful for the determination of vanadium in steels and various alloys (20, 23). It was hoped to apply this spectrophotometric system to vanadium in niobium metal. However, it was found that the presence of citrate, tartrate, or other complexing reagents necessary for keeping the niobium in solution interfered with the color forming reagent. Therefore, it was not possible to determine vanadium

directly in niobium metal. A phosphotungstate method (for vanadium) was not readily applicable to this particular matrix (1).

After removal of niobium and tantalum by ion exchange, the vanadium can be determined easily by a spectrophotometric procedure. The N-phenylbenzohydroxamic acid procedure was tested by addition of 5 micrograms of vanadium to a solution containing 1 gram of powdered material to (100 M x D) which contained 4 p.p.m. of vanadium by the ion exchange emission spectrographic technique. The concentration of vanadium found in the blank (Material 2) was 4.5 p.p.m. and that found in the "spiked" sample was 9.5 p.p.m. This corresponds to a recovery of 5.0 p.p.m. of the vanadium or 100% of the amount added. Since the sensitivity is not as good as the emission spectrographic method, the spectrophotometric procedure was used mostly as another method for verification and support of results obtained by the spectrograph.

b. Emission Spectrographic Methods

(1) Aluminum

Spectrophotometric methods for trace concentrations of aluminum (<50 p.p.m.) are unreliable; therefore, no development work with this technique was considered. Existing emission spectrographic methods were not sensitive below 30 p.p.m.; therefore, modification of the existing method was required.

It was necessary to prepare a set of standards for the trace aluminum determination. To make these standards a source of niobium oxide whose aluminum content was less than the samples to be analyzed was required. Niobium oxide prepared by an ion exchange technique was tried, but the aluminum content was not significantly less than that of the three samples of niobium metal. A systematic search of two to three dozen samples of competitive brands and miscellaneous experimental lots resulted in the selection of a batch of oxide with requisite purity for the preparation of the standards.

In the initial search for Nb₂O₅ of low aluminum content, it soon became apparent that the DC arc technique for higher aluminum contents was unsuitable for trace aluminum analyses both in regard to sensitivity and precision. A highly sensitive and valuable double cap mix technique and AC arc excitation was therefore devised and utilized in both the search for low-aluminum Nb₂O₅ and in quantitative analytical work on the special samples.

(2) Silicon

Spectrophotometric methods are unreliable for silicon in niobium metal below 100 p.p.m. Again, the emission spectrographic method required modification for silicon in the range of interest (less than 10 p.p.m.). The trace silicon determination required the preparation of special standards. An unsuccessful attempt was made to purify Nb₂O₅ by treatment with hydrofluoric and sulfuric acids and evaporation to dryness. Similar to the case of the trace aluminum determination the problem of acquiring oxide of requisite purity was solved by testing many miscellaneous samples of Nb₂O₅ until one of requisite purity was found.

Greater care is necessary in the preparation of p.p.m. silicon standards than in the case for other elements. The boron carbide mortar used in grinding and mixing the oxide will contribute silicon unless care is used. Hand grinding with an acetone slurry was effective in minimizing the contamination from this source. The 1% GeO_2 , 0.25% PdCl_2 graphite-oxide mix used in the regular method was not used in the trace silicon method. This is because a small amount of silicon contamination results from the preparation of this mix probably from the thorough grinding and mixing operation. Because the silicon is almost completely removed from the graphite-oxide mix during the period of exposure (total energy method) and a set of standards are included on each plate, the precision of the analysis is still adequate (about $\pm 10\%$).

The accuracy of the method cannot readily be determined. However, one of high standards was analyzed using the GeO_2 mix with the high range method. The result plotted well on the high range curve indicating that a continuity exists between the two methods.

(3) Zirconium, Titanium, Vanadium, and Tin

Preliminary analysis of the niobium metals indicated that the concentrations of zirconium, titanium, vanadium and tin were too low for determination of these traces directly on the oxide of the metal. Spectrographic standards and working curves prepared by dry-grinding various elements in both a niobium and tantalum oxide matrix were available in the laboratory. These had been prepared in prior years and were based on more than one set of dry-ground standards each containing zirconium, vanadium, titanium, and tin together with different combinations of other elements. Analysis with these curves had demonstrated that greater sensitivity and better precision for the zirconium determination was possible when measurement was made in a Ta_2O_5 matrix rather than a Nb_2O_5 matrix. Thus, when separation techniques were considered, it was decided to use tantalum as a carrier and measure the elements in a Ta_2O_5 matrix.

To check the accuracy of the dry-ground standards, additional standards were prepared for titanium, vanadium, and zirconium by the addition of known concentrations of these elements to a solution containing a known amount of tantalum and then precipitating with cupferron, filtration, and ignition to the oxide. In every case these new standards plotted in close agreement with the data from the existing working curves. The existing working curves for tin were used without the preparation of check standards because of insufficient time and urgency to investigate this method completely.

The tantalum used as a collector must be of high purity with respect to these elements as well as niobium. If none is available, it may be prepared by ion-exchange separation of all these elements from the tantalum and then selective elution of the tantalum and collection of this fraction in a plastic bottle for future use as a collector.

(4) Lithium

The qualitative examination showed that only one vendor's niobium metal contained lithium. A single set of standards was prepared by dissolving lithium-free metal with hydrofluoric acid, adding appropriate amounts of a lithium standard solution and evaporating to dryness in the presence of sulfuric acid. The samples were prepared in a similar manner. A sensitive spark solution method was tried as an alternative check method but did not have sufficient sensitivity.

For details of the methods see Appendix II.

V. SUMMARY OF ANALYTICAL METHODS

Details of the analytical methods for the analysis of niobium metal for this project and Task A Activity 6 are given in Appendix I, II, and III for the spectrophotometric, emission spectrographic, and miscellaneous methods. A short description of each method and the estimated lower limit of detectability appears in Table V.

TABLE V

METHOD AND LOWER LIMIT OF DETECTABILITY FOR ANALYSIS OF
TRACE ELEMENTS IN NIOBIUM METAL

<u>Element</u>	<u>Procedure</u>	<u>Lower Limit of Detect- ability (ppm)</u>	<u>Description of the Method</u>
C	Combustion- Conductometric	5 to 10	Combustion of sample in oxygen at 1400°C. collection of CO ₂ in strontium hydroxide solution, and conductometric determination of the CO ₂ concentration.
O	Vacuum Fusion	5 to 10	Fusion of the sample in a platinum bath, collection and measurement of the CO ₂ .
H	Vacuum Fusion	1	Fusion of the sample in a platinum bath, collection and measurement of the hydrogen.
N	a. Distillation- titrimetric b. Distillation- spectrophotometric	50 1	(The metal is dissolved in a medium for (conversion of nitrides to the ammonium (salt, distillation of ammonia, and (titrimetric or spectrophotometric deter- (mination of the ammonia.
B	Emission Spectrographic	0.2	The metal is ignited to the oxide, mixed with gallium oxide, and the mixture excited using the carrier distillation technique.
Al	Emission Spectrographic	3	The metal is ignited to the oxide, mixed with graphite and determined by using an AC arc, double cap mix technique.

Element	Procedure	Lower Limit of Detect- ability (ppm)	Description of the Method
Ca	Emission Spectrographic	30	Nb ₂ O ₅ prepared from the metal is mixed with graphite and excited with a high-voltage AC spark and a cap mix technique.
Cr	Spectrophotometric	1	After dissolution, the niobium is separated from the chromium by an extraction of niobium cupferrate with chloroform. The chromium is determined spectrophotometrically in the aqueous phase with diphenyl carbazide.
Co	Spectrophotometric	5	After dissolution, the niobium is separated from the cobalt by an extraction of niobium cupferrate with chloroform. The cobalt is determined spectrophotometrically in the aqueous phase with tetraphenylarsonium chloride.
Cu	Spectrophotometric	1	After dissolution of the metal, the copper is reduced with hydroxylamine hydrochloride, the complex with neocuproine extracted with chloroform and measured spectrophotometrically (2, 18).
Fe	Spectrophotometric	1	After dissolution of the metal, the iron is reduced, the complex with bathophenanthroline extracted with chloroform, and the colored solution measured spectrophotometrically (3).
Li	Emission Spectrographic	3	The metal is dissolved in acids, acids volatilized, residue mixed with graphite and excited in a direct-current arc.
Mg	Emission Spectrographic	30	Nb ₂ O ₅ prepared from the metal is mixed with graphite and excited with a high-voltage AC spark and a cap mix technique.
Mn	Spectrophotometric	1	After dissolution of the metal, the niobium cupferrate is extracted with chloroform, and the manganese oxidized with KIO ₄ to permanganate which is measured spectrophotometrically.
Mo	Spectrophotometric	1	After dissolution of the metal, the molybdenum thiocyanate complex is extracted with butyl acetate and the color measured spectrophotometrically.

<u>Element</u>	<u>Procedure</u>	<u>Lower Limit of Detect- ability (ppm)</u>	<u>Description of the Method</u>
Ni	Spectrophotometric	1	The metal is dissolved, copper removed with neocuproine, and the nickel dimethylglyoxime complex extracted with chloroform. Nickel back extracted in an acid solution and the nickel determination spectrophotometrically with dimethylglyoxime.
Si	Emission Spectrographic	2	The metal is converted to oxide, mixed with graphite and the sample excited in a DC arc.
Ta	a. Spectrophotometric	100	After dissolution of the metal and removal of traces of boron, the tantalum is extracted from an oxalate solution as the methylviolet-fluoride complex with benzene (7).
	b. Spectrophotometric	5	An HF-HCl solution of the metal is passed through an anion exchange column. After eluting the column with a special solution to remove most of the niobium, the ion exchange material is ignited, the residue containing the tantalum fused, and the melt dissolved in ammonium oxalate solution. The tantalum is determined spectrophotometrically as the methyl violet fluoride complex in benzene.
Sn	a. Spectrophotometric	3	The metal is dissolved, tin extracted with (2-ethylhexyl) phosphine oxide into cyclohexane, and the color developed with pyrocatechol violet.
	b. Emission Spectrographic	0.5	See titanium (emission spectrographic).
Ti	a. Emission Spectrographic	0.5	An HF-HCl solution of the metal is passed through an anion exchange column to separate the titanium from niobium. The titanium is precipitated as cupferrate with tantalum as carrier, and ignited to the oxide. The oxide is mixed with graphite, GeO_2 , and PdCl_2 and excited in a DC arc. The same procedure is applicable for V, Sn, and Zr.
	b. Spectrophotometric	0.5	An HF-HCl solution of the metal is passed through an anion exchange column to separate the titanium from niobium. The titanium is determined spectrophotometrically in the eluate by extraction of the thiocyanate complex by TOPO in cyclohexane.

<u>Element</u>	<u>Procedure</u>	<u>Lower Limit of Detect- ability (ppm)</u>	<u>Description of the Method</u>
V	Emission Spectrographic	0.5	See Ti (emission spectrographic)
Zr	a. Emission Spectrographic	0.5	See Ti (emission spectrographic)
	b. Spectrophotometric	0.5	An HF-HCl solution of the metal is passed through an anion exchange column to separate the zirconium from the niobium. The zirconium is determined spectrophotometrically in the eluate with phenylfluorone.
W	Spectrophotometric	1	After dissolution of the metal and removal of any Mo present with dithiol, the W is reduced with Ti (III) and the complex with dithiol extracted with amylacetate and measured spectrophotometrically (7, 11).

VI. CONCLUSIONS

1. Three types of niobium metal, made by different manufacturing processes, were reduced to powder and their chemical compositions determined in detail. Analyses were made for trace elements that are suspected to influence capacitor properties. The compositions are reported in Table III.

2. New analytical methods were developed for the determination of less than 20 p.p.m. of the elements titanium, aluminum, silicon, vanadium, tin, and zirconium. These methods are given in detail in the Appendices of the report.

VII. REFERENCES

1. Cooper, M. D. and Winter, P. K., Anal. Chem., 21, 605 (1949).
2. Gahler, A. R., Anal. Chem. 26, 577 (1954).
3. Gahler, A. R., Hamner, R. M., and Shubert, R. C., Anal. Chem. 33, 1937 (1961).
4. Green, H. J., British Cast Iron Res. Assn., 10, 586 (1962).
5. Green, H., Metallurgia, 65, 305 (1962).
6. Greenberg, P., Anal. Chem. 29, 896 (1957).
7. Greenberg, P. and Smart, A., Anachem Conference, Detroit, Michigan, Oct. 1960.
8. Hahn, R. B. and Johnson, J. L., Anal. Chem. 29, 902 (1957).
9. Hague, J. L., Brown, E. D., and Bright, H. A., J. of Research, Nat'l. Bur. Standards 53, 261 (1954).
10. Hague, J. L. and Machlan, L. A., J. of Res., NBS, 62, 53 (1959).
11. Hobart, E. W. and Hurley, E. P., Anal. Chim. Acta., 27, 144 (1962).
12. Kallmann, S., Oberthim, H., and Liu, R., Anal. Chem. 34, 609 (1962).
13. Luke, C. L., Anal. Chem. 31, 1803 (1959).
14. Milner, G. W. C. and Edwards, J. W., Anal. Chim. Acta. 13, 230 (1955).
15. Moore, F. L., Anal. Chem. 28, 997 (1956).
16. Onishi, H. and Sandell, E. B., Anal. Chim. Acta 14, 153 (1956).
17. Ovenston, T. C., Analyst 80, 566 (1955).
18. Penner, E. M. and Inman, W. R., Talanta 10, 407 (1963).
19. Polyak, L. Ya., Z. Anal. Khim (USSR), 17, 206 (1962) English Translation.
20. Priyadarshini, U. and Tandon, S. C., Anal. Chem. 33, 435 (1961).
21. Ross and White, Anal. Chem. 33, 421 (1961).
22. Ross and White, ibid., 33, 424 (1961).
23. Ryan, D. E., Analyst 85, 569 (1960).
24. Yoe, J. H. and Armstrong, A. R., Anal. Chem., 19, 100 (1947).
25. Zharovskii, F. G. and Pilipenko, A. T., Zarodskaya Laboratoria, 23, 1407 (1957).
See also Analytical Abstracts 5, 294P (1958).

VIII. CONTRIBUTING PERSONNEL

The following personnel contributed to the work reported:

C. M. Brown)
H. J. Brown) Refractory Metals Department

W. P. Evans)
A. R. Gahler)
P. Greenberg)
R. M. Hamner) Technology Analytical Laboratory
F. S. Jones)
J. F. Langkau)
R. A. Lannoye)

A. R. Gahler
A. R. Gahler

ARG:djh

APPENDICES I - III

APPENDIX I - SPECTROPHOTOMETRIC METHODS

DETERMINATION OF CHROMIUM IN NIOBIUM METAL (PHOTOMETRIC WITH DIPHENYLCARBAZIDE)

SCOPE

This procedure is designed for the determination of 1 to 100 p.p.m. of chromium in niobium metal.

PRINCIPLE OF METHOD

The metal is dissolved in HF and HNO₃, and the niobium cupferrate extracted with chloroform. After evaporation, the chromium is oxidized with ammonium persulfate, (NH₄)₂S₂O₈, in the presence of AgNO₃ and determined photometrically as the diphenylcarbazide complex.

CONCENTRATION RANGE

The range of the method at 540 mμ using 5-cm. cells is 0 to 20 micrograms of chromium per 100 ml. The range can be extended to determine up to 100 micrograms (0.1 mg.) of chromium per 100 ml. by preparing a suitable absorbance-concentration curve using 1-cm. cells. The colored system follows Beer's law but is not stable, so the absorbance should be measured as described in the procedure.

INTERFERENCES

There are no interferences from other metal ions in the concentrations normally found in niobium metal. Up to one mg. of iron can be tolerated without interference. A slight turbidity due to niobium may be removed by centrifuging the colored solution just before photometric measurement.

SPECIAL REAGENTS

3N H₂SO₄ + 1:5N H₃PO₄ Mixture - Mix 166 ml. of H₂SO₄ (1:1) and 100 ml. of 85% H₃PO₄, and dilute to one liter. Heat, add 0.01N KMnO₄ solution dropwise to the hot acid until a faint color appears. Store in a glass stoppered bottle.

Sodium Hydroxide (100 g./liter) - Dissolve 50 g. of reagent grade pellets in 500 ml. of water. Store in a polyethylene bottle.

Silver Nitrate (0.5 g./liter) - Dissolve 50 mg. of the salt in 100 ml. of water. Store in a brown glass dropping bottle.

Potassium Permanganate (2 g./liter) - Dissolve 0.2 g. of the salt in 100 ml. of water. Store in a brown glass dropping bottle.

Diphenylcarbazide (0.2 g./100 ml.) - Dissolve 0.2 g. of the reagent in 100 ml. of 95% ethanol. Prepare fresh daily and store in a refrigerator.

Standard Chromium Solution - Dissolve 0.2829 g. of N.B.S. potassium dichromate in water and dilute to one liter. One ml. = 0.1 mg. of chromium. Dilute a 10-ml. aliquot of this stock solution to 500 ml. One ml. = 0.002 mg. (2 micrograms) of chromium.

SPECIAL APPARATUS

A spectrophotometer capable of utilizing 5-cm. cells.

SPECIAL PRECAUTIONS

All the glassware used in this determination must be thoroughly cleaned. The beakers should be boiled with nitric and perchloric acids, fumed strongly with perchloric acid, and thoroughly rinsed with distilled water. It is advisable to set aside glassware to be used exclusively for this determination. To obtain a low blank, it may be necessary to pass the distilled water through an ion-exchange column and store in a Pyrex bottle.

PREPARATION OF CALIBRATION GRAPH

Pipet 0 (blank), 1-, 2-, 5-, 7-, and 10-ml. aliquots of the standard chromium solution (one ml. = 2 micrograms of chromium) into 100-ml. Pyrex volumetric flasks. Dilute to about 50 ml. Add 10 ml. of the $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ acid mixture. Add 3 drops of the AgNO_3 solution, one drop of KMnO_4 solution, and 0.2 g. of $(\text{NH}_4)_2\text{S}_2\text{O}_8$. Wash down the neck of the flask and add a Hengar (Al_2O_3) boiling chip. Boil gently for 30 minutes to assure complete oxidation of the chromium and decomposition of the excess ammonium persulfate. The faint pink color of the permanganate should remain throughout the entire boiling period (Note 1). Cool to room temperature, add from a pipet 10 ml. of the diphenylcarbazide reagent, dilute to the mark with water, and mix. Measure the absorbance within 10 minutes on a spectrophotometer at 540 m μ in 5-cm. cells using the blank as reference solution. Plot absorbance versus micrograms of chromium per 100 ml.

PROCEDURE

Carry a blank through the entire procedure.

Dissolve 1.000 g. of niobium metal in a 100-ml. platinum dish fitted with a platinum cover, using 5 ml. of HF and dropwise addition of HNO_3 . Add 10 ml. of H_2SO_4 and evaporate to light fumes of H_2SO_4 . Cool and add HF dropwise to obtain a clear solution. Transfer the sample to a polyethylene beaker containing 50 ml. of HF (2:98) solution. Rinse the platinum dish with HF (2:98) solution and add to the main solution. Chill the sample solution, the cupferron solution (saturated solution in water), and the chloroform to between 0 and 5°C. (Note 2).

Transfer the sample to a chilled, 250-ml. separatory funnel containing 50 ml. of the chilled cupferron suspension. Mix, add 100 ml. of the chilled chloroform and shake one minute. Withdraw the organic layer and discard. Add cupferron, about 5 ml. at a time until precipitation is complete. Repeat the extraction with 30 to 40 ml. of chloroform until the lower layer is colorless. Rinse the funnel stem with chloroform, then with water. Add 50 ml. of isopropyl ether and shake one minute.

Withdraw the aqueous layer containing the chromium to a 250-ml. Teflon beaker and evaporate to 50 ml. or less. Add 20 ml. of HCl and 10 ml. of HNO_3 , cover partially, and evaporate to remove ammonium salts and HF (Note 3). Cool, transfer to a 150-ml. Pyrex beaker, and evaporate to about one ml. of H_2SO_4 . Dilute to 25 ml. and neutralize with NaOH solution (pH paper). Add 10 ml. of $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ acid mixture

DETERMINATION OF COBALT IN NIOBIUM METAL
(PHOTOMETRIC WITH TETRAPHENYLARSONIUM
CHLORIDE AND THIOCYANATE)

SCOPE

This method is designed for the determination of 5 to 100 p.p.m. of cobalt in niobium metal.

PRINCIPLE OF METHOD

The metal is dissolved in HF and HNO₃, fumed in H₂SO₄, and the niobium cupferrate extracted with chloroform. After evaporation of the aqueous phase, thiosulfate, thiocyanate, and fluoride are added to the sample. Tetraphenylarsonium chloride is added to form the blue tetraphenylarsonium cobaltthiocyanate complex which is extracted with chloroform and measured at 620 mμ.

CONCENTRATION RANGE

The range using 5-cm. cells is from 5 to 100 micrograms of cobalt in 25 ml. of chloroform. The system follows Beer's law and is stable for at least 24 hours. The range can be extended to determine up to 0.02% cobalt by preparing an absorbance-concentration graph using 1-cm. cells.

INTERFERENCES

There are no interferences from other metal ions in the concentrations normally found in niobium metal.

A slight turbidity due to niobium may be removed by centrifuging the colored solution just before photometric measurement.

SPECIAL REAGENTS

Tetraphenylarsonium Chloride - Dissolve 2.28 g. of the salt in 100 ml. of water. (Obtainable from A. D. McKay, Inc., or Eastern Chemicals Company.)

Sodium Thiosulfate - Dissolve 10 g. of the salt in water and dilute to 100 ml. Prepare fresh for each determination.

Ammonium Thiocyanate - Dissolve 50 g. in water and dilute to 100 ml.

Standard Cobalt Solutions

a. Stock Solution - Dissolve 1.00 g. of cobalt metal in 30 ml. of HNO₃ (1:1). Add 10 ml. of sulfuric acid and take to fumes to remove the nitric acid. Cool, dilute to about 100 ml., heat to dissolve the salts, cool, and dilute to one liter with water.

b. Dilute Standard Cobalt Solution - Transfer 10 ml. of the stock solution to a liter volumetric flask and dilute to volume (one ml. of solution equals 0.01 mg. of cobalt).

PREPARATION OF CALIBRATION GRAPH

Transfer 0 (blank), 1-, 2-, 5-, 7-, and 10-ml. aliquots of the dilute standard cobalt solution (one ml. equals 10 micrograms of cobalt) to 150-ml. beakers. Dilute to 25 ml. and adjust the acidity by adding NH_4OH until just alkaline, then dropwise HCl until just acid (pH paper).

Add successively with stirring 2 to 3 drops of sodium thiosulfate solution, 5 ml. of ammonium thiocyanate solution, and 0.05 g. of ammonium fluoride. Transfer to a 125-ml. separatory funnel using a small amount of water. Add 10 drops of tetraphenylarsonium chloride solution and mix. Extract with 10 ml. of chloroform by shaking one minute. Withdraw the chloroform layer through a loosely fitted cotton plug in the funnel stem into a 25-ml. volumetric flask. Repeat the extraction twice more using 5-ml. portions of chloroform and 2 drops of tetraphenylarsonium chloride. The last extract should be colorless. Dilute to volume with chloroform. Measure the absorbance at 620 $\text{m}\mu$ in 5-cm. cells using the blank as reference solution. Plot absorbance versus micrograms of cobalt per 25 ml.

PROCEDURE

Carry a blank through the entire procedure.

Dissolve 1.000 g. of niobium metal in a 100-ml. platinum dish fitted with a platinum cover, using 5 ml. of HF and dropwise addition of HNO_3 . Add 10 ml. of H_2SO_4 and evaporate to light fumes of H_2SO_4 . Cool and add HF dropwise to obtain a clear solution. Transfer the sample to a polyethylene beaker containing 50 ml. of HF (2:98) solution. Rinse the platinum dish with HF (2:98) solution and add to the main solution. Chill the sample solution, the cupferron solution (saturated solution in water), and the chloroform to between 0 and 5°C. (Note 1).

Transfer the sample to a chilled, 250-ml. separatory funnel containing 50 ml. of the chilled cupferron suspension. Mix, add 100 ml. of the chilled chloroform, and shake one minute. Withdraw the organic layer and discard. Add cupferron, about 5 ml. at a time until precipitation is complete. Repeat the extraction with 30 to 40 ml. of chloroform until the lower layer is colorless. Rinse the funnel stem with chloroform, then with water. Add 50 ml. of isopropyl ether and shake one minute.

Withdraw the aqueous layer containing the cobalt to a 250-ml. Teflon beaker and evaporate to 50 ml. or less. Add 20 ml. of HCl and 10 ml. of HNO_3 , cover partially, and evaporate to remove ammonium salts and HF (Note 2). Cool, transfer to a 150-ml. Pyrex beaker, and fume to about one ml. of H_2SO_4 or less. Dilute to 25 ml. and neutralize with NH_4OH , then add HCl dropwise until just acid (pH paper). Continue as described in Preparation of Calibration Graph, starting with "Add successively with stirring 2 to 3 drops...." (Note 3).

NOTES

1. If the temperature of the solution is not less than 5°C., the niobium cupferrate is only slightly soluble. The cupferron solution should be freshly prepared, nearly colorless, and should contain some undissolved reagent.

2. If the solution turns black, add HNO_3 dropwise and repeat the fuming. Continue adding HNO_3 and evaporating to fumes until all organic matter is destroyed.

3. If the depth of color is beyond the range of 5-cm. cells, measure the absorbance in 1-cm. cells and refer to the proper calibration graph.

DETERMINATION OF COPPER AND NICKEL IN NIOBIUM METAL
(PHOTOMETRIC WITH NEOCUPROINE AND DIMETHYLGLYOXIME)

SCOPE

This method is suitable for the determination of copper and nickel in niobium metal within the range of 1 to 100 p.p.m.

PRINCIPLE OF METHOD

After dissolution of the sample in HF and HNO₃ and removal of excess HF with H₂SO₄, the niobium is complexed with ammonium citrate. The pH is adjusted to 5 to 7 with NH₄OH, and copper is extracted as the neocuproine complex with chloroform and determined spectrophotometrically. The aqueous phase from the copper separation is adjusted to pH 9 and nickel is extracted as the dimethylglyoxime complex with chloroform. After back-extracting with HCl, nickel is determined spectrophotometrically with dimethylglyoxime.

CONCENTRATION RANGE

The colored systems follow Beer's law in the range from 1 to 40 micrograms of copper and 1 to 20 micrograms of nickel in 25-ml. volume using 5-cm. cells. The range may be extended by using 1-cm. cells. The sensitivity for copper can be doubled by substitution of the more sensitive reagent, bathocuproine, for neocuproine (Note 1).

INTERFERENCES

There are no interferences in this procedure as written. If nickel is to be determined but not copper, then the copper must be removed before the nickel dimethylglyoxime extraction. If a high blank is obtained, it may be necessary to use redistilled or ion-exchange water.

SPECIAL REAGENTS

Ammonium Citrate - Dissolve 400 g. of diammonium citrate in 700 ml. of water. Adjust to a pH of 9 to 9.5 with ammonium hydroxide and transfer to a one-liter separatory funnel. Add 10 ml. of dimethylglyoxime solution and make three extractions with 30-ml. portions of chloroform. Filter and dilute to one liter.

Hydrochloric Acid, 0.5N - Dilute 40 ml. of reagent grade HCl to one liter.

Hydroxylamine Hydrochloride Solution - Dissolve 50 g. of NH₂OH·HCl in 500 ml. of water.

Neocuproine Solution - Dissolve 0.5 g. of neocuproine (2,9-dimethyl-1,10-phenanthroline, G. F. Smith Chemical Company) in 500 ml. of 95% ethanol.

Dimethylglyoxime - Dissolve one gram of recrystallized dimethylglyoxime in 500 ml. of 95% ethanol. To recrystallize the dimethylglyoxime, dissolve the dimethylglyoxime in absolute ethanol. Warm gently until the dimethylglyoxime is in solution. Chill until the dimethylglyoxime recrystallizes. Filter on a fritted crucible and allow to air-dry. If the colored system is not stable for at least one-half hour, repurify the reagent.

Standard Copper Solution - Dissolve 0.200 g. of high-purity copper wire in 5 ml. of HNO_3 (1:3). Add 10 ml. of H_2SO_4 (1:1) and 5 ml. of formic acid, and evaporate to fumes. Cool and dilute to one liter. Dilute 10.0 ml. of this stock solution to one liter (one ml. = 2 micrograms of copper).

Standard Nickel Solution - Dissolve 0.200 g. of high-purity nickel metal in 5 ml. of HNO_3 (1:1). Add 10 ml. of H_2SO_4 (1:1) and 5 ml. of formic acid, and evaporate to fumes. Cool and dilute to one liter. Dilute 10.0 ml. of this stock solution to one liter (one ml. = 2 micrograms of nickel).

PREPARATION OF COPPER ABSORBANCE-CONCENTRATION GRAPH

Transfer 0 (blank), 1-, 2-, 5-, 7-, and 10-ml. aliquots of the diluted copper stock solution to 125-ml. separatory funnels. Add 10 ml. of hydroxylamine-hydrochloride solution, 5 ml. of ammonium citrate solution, and dilute to 25 ml. Adjust the pH to 6 with NH_4OH (pH paper). Add 5 ml. of neocuproine, mix, and add 10-ml. of chloroform. Shake one minute and withdraw the organic phase into a 25-ml. volumetric flask containing 2 ml. of 95% ethanol. Make another extraction with 5 ml. of chloroform. Dilute to the mark with ethanol and mix. Measure the absorbance at 476 $\text{m}\mu$ using 5-cm. cells and the reagent blank as reference solution. Plot absorbance versus micrograms of copper per 25 ml.

PREPARATION OF NICKEL ABSORBANCE-CONCENTRATION GRAPH

Transfer 0 (blank), 1-, 2-, 5-, 7-, and 10-ml. aliquots of the diluted nickel stock solution to 25-ml. volumetric flasks. Add 2 drops of HCl , 3 drops of bromine water, and dilute to 15 ml. Add NH_4OH dropwise until the bromine color is discharged and then 4 drops of excess. Add 5 ml. of dimethylglyoxime solution immediately, dilute to the mark with water, and mix. After standing 5 minutes, measure the absorbance at 450 $\text{m}\mu$ using 5-cm. cells and the reagent blank as reference solution. Plot absorbance versus micrograms of nickel per 25 ml.

PROCEDURE

I. DISSOLUTION OF NIOBIUM METAL

Transfer one gram of sample to a 100-ml. platinum dish or 250-ml. Teflon beaker fitted with a cover. Carry a blank through the procedure. Add 10 ml. of HF and a few drops of HNO_3 to complete the dissolution. Add more HNO_3 and warm, if necessary. Add 10 ml. of H_2SO_4 , 2 ml. of formic acid, mix, and evaporate at low heat until H_2SO_4 fumes begin to evolve (Note 2). Cool to room temperature, add 10 ml. of ammonium citrate solution, stir and transfer to a 250-ml. beaker. Polish the platinum dish and wash into the beaker. Adjust the pH of the sample solution to 6 with NH_4OH (pH paper), dilute to 60 ml., and boil to obtain a clear solution. Determine the copper and nickel as described under Sections II and III. If nickel is to be determined and not copper, the separation of copper must be made since copper interferes in the nickel determination.

II. DETERMINATION OF COPPER

Transfer the sample solution containing not more than 50 micrograms of copper or 20 micrograms of nickel to a 125-ml. separatory funnel (Note 3). Add 10 ml. of hydroxylamine-hydrochloride solution, mix, and adjust the pH between pH 5-7.

Add 5 ml. of neocuproine solution, mix, and add 10 ml. of chloroform. Shake one minute and allow to separate. Withdraw the organic layer into a 25-ml. volumetric flask containing 2 ml. of ethanol. Extract again with 5 ml. of chloroform to ensure complete removal of copper and reagent. Dilute to the mark with ethanol and mix. Measure the absorbance at 476 m μ using 5-cm. cells and the reagent blank as reference solution. Determine the concentration of copper from the previously established calibration graph.

III. DETERMINATION OF NICKEL

Adjust the aqueous phase in the separatory funnel from the copper separation to pH 9 by dropwise addition of NH_4OH . Add 5 ml. of dimethylglyoxime solution and shake one-half minute. Add 10 ml. of chloroform and shake 2 minutes. Separate and withdraw the organic layer into another separatory funnel containing 10 ml. of HCl (0.5N). Repeat the extraction twice more with 5-ml. portions of chloroform and add these to the separatory funnel containing the first chloroform fraction. Discard the aqueous phase.

Shake the combined fractions for one-half minute with the 0.5N acid. Withdraw the organic phase into another separatory funnel. Rinse the aqueous phase into a 150-ml. beaker. Repeat the extraction twice more with 5-ml. portions of 0.5N HCl , and transfer the HCl extracts to the 150-ml. beaker.

Insert a boiling rod in the 150-ml. beaker and boil the HCl extracts for 10 minutes. Add 5 ml. of bromine water and continue boiling until the volume is reduced to 5 ml. or less. Cool in a water bath and transfer to a 25-ml. volumetric flask. Complete the determination as described under Preparation of Nickel Absorbance-concentration Graph, starting at "add 3 drops of bromine water...." Determine the concentration of nickel from the calibration graph.

NOTES

1. Determination of nickel subsequent to extraction of copper with bathocuproine has not been tested.

2. Formic acid is added to decompose HNO_3 . Use care to avoid spray loss. Do not evaporate to dense fumes of H_2SO_4 . Add 1 or 2 drops of HF , if necessary, to clear the solution.

3. If the sample is known to contain more than 40 and 20 micrograms of copper or nickel, respectively, dilute to volume and obtain a suitable size aliquot. Alternatively, the absorbance may be measured in 1-cm. cells, if the concentration of copper or nickel is not greater than 100 micrograms. In this case prepare a calibration graph for the range of 10 to 100 micrograms using 1-cm. cells.

DETERMINATION OF IRON IN NIOBIUM METAL
(SPECTROPHOTOMETRIC WITH BATHOPHENANTHROLINE)

SCOPE

This method is designed especially for the determination of traces of iron in high-purity niobium metal, although the method as written is applicable to iron 1 p.p.m. or as high as 2%.

PRINCIPLE OF METHOD

The metal is dissolved in HF and HNO₃, the HNO₃ is removed by evaporation in the presence of formic acid. After reduction of the iron with sodium hydrosulfite, the iron (II) bathophenanthroline complex is extracted with a chloroform-ethanol solution, and the absorbance of the orange-red colored system measured at 536 mμ.

CONCENTRATION RANGE

The range extends from 0.002 to 0.12 mg. of iron in 50 ml. of organic solvent using 1-cm. cells.

INTERFERENCES

None of the constituents present in niobium metal interfere with the method. Large amounts of copper, nickel, manganese, or cobalt which would not ordinarily be found in niobium would interfere (Note 1).

SOLUTIONS AND REAGENTS

Bathophenanthroline (4,7-Diphenyl-1,10-Phenanthroline) - G. F. Smith Chemical Company, Columbus, Ohio - Dissolve 0.1 gram of the reagent in 100 ml. of 95% ethanol. Stir well to dissolve. The solution is stable indefinitely.

Sodium Citrate Solution - Dissolve 100 grams of sodium citrate in one liter of distilled water. Adjust the pH to 5.0 by addition of citric acid. Iron is removed by addition of 3 ml. of 2% cupferron solution to about 150 ml. of the sodium citrate solution in a separatory funnel, allowing to stand a few minutes, and extraction of the iron cupferrate with about 25 ml. of chloroform. Repeat the extraction with chloroform 3 to 4 times to remove all the metal cupferrates and the excess cupferron. A final extraction with 50 ml. of diisopropyl ether aids in extraction of the cupferron.

Sodium Hydrosulfite (also known as sodium dithionite) (Na₂S₂O₄) - Prepare FRESH just before use. Dissolve 10 grams of sodium hydrosulfite in 100 ml. of water. Transfer to a separatory funnel and remove the iron by addition of 10 ml. of bathophenanthroline solution and extraction of the complex with 15 ml. of chloroform. Repeat the chloroform extraction until the chloroform solution remains colorless after extraction. The hydrosulfite solution should not stand more than one-half hour before use.

Standard Iron Solutions

A. Stock Iron Solution (1 ml. of Solution = 1 mg. of Iron) - Dissolve 0.1 gram of high-purity iron metal in 10 ml. of hydrochloric acid. Add 2 ml. of nitric acid and evaporate to near dryness. Add 5 ml. of HCl and dilute to 100 ml. in a volumetric flask.

B. Diluted Standard Iron Solution (1 ml. of solution = 0.01 mg. of Iron) - Transfer 5 ml. of the iron stock solution to a 500-ml. volumetric flask. Add 25 ml. of HCl and dilute to the mark with distilled water.

Sodium Hydroxide (100 g./liter) - Dissolve 50 grams of sodium hydroxide in 500 ml. of water. Add 5 ml. of $MgCl_2$ (100 g./liter) solution, stir for 2 minutes, and heat just below boiling for 10 minutes. Let stand for 15 minutes and filter through Whatman No. 41H paper into a 500-ml. polyethylene container.

PREPARATION OF CALIBRATION CURVE

Place 1-, 2-, 5-, and 10-ml. aliquots of the diluted standard iron solution into separatory funnels. Carry a blank along with the samples. Add 25 ml. of distilled water and 20 ml. of the sodium citrate solution, adjust the pH of the solution with ammonium hydroxide to between 4 and 6 (Note 2), and then add 20 ml. of the fresh pre-extracted sodium hydrosulfite solution. Mix between addition of reagents and allow to stand 15 minutes after the sodium hydrosulfite addition to reduce the iron. Add 10 ml. of the bathophenanthroline reagent and then 15 ml. of chloroform. Shake for 30 seconds, allow the phases to separate, and draw off the chloroform layer into a 50-ml. volumetric flask previously rinsed with 95% ethanol. Add 10 ml. of chloroform to the separatory funnel and repeat the extraction. Dilute the combined chloroform extracts in the 50-ml. volumetric flask to the mark with 95% ethanol. Mix and read the absorbance of the solutions with the blank in the reference beam of the spectrophotometer at 533 m μ in a 1-cm. cell. Plot absorbance versus concentration. The system follows Beer's law.

APPARATUS

Any photoelectric measuring device.

PROCEDURE

Dissolve 1.0 gram of niobium metal (Note 3) in 10 ml. of HF (1:1) and dropwise addition of HNO_3 (15 to 20 drops). Carry a blank on the reagents along with the samples. Evaporate until the niobium begins to hydrolyze, remove from the heat, cool, and add 5 ml. of HF and 2 ml. of formic acid. Evaporate to a volume of 2 or 3 ml., add 30 ml. of the sodium citrate solution, and heat until all the sample is complexed with the citrate. Dilute with 20 ml. of water and cool. Transfer the sample to a separatory funnel containing 10 ml. of 4.5% boric acid. If the pH of the solution is not pH 5, adjust with NH_4OH , and proceed as described in the Preparation of Calibration Curve.

NOTES

1. Copper interference is eliminated by extracting at a pH range of 4 to 6. However, if copper is present in concentrations greater than 10 times the iron content, the copper must be removed. A previous extraction with neocuproine would

be convenient. Cobalt (1 mg.) can be tolerated if the bathophenanthroline reagent volume is increased from 10 to 20 ml. At least 2.0 mg. of nickel and 10 mg. of manganese may be present.

2. The pH of the solution should not be below 4 in order to prevent the formation of colloidal sulfur in the aqueous phase.

3. The method as described is directly applicable for iron in the 0.0005 to 0.012% range. Outside this range, the sample size, dilution volume, or aliquot taken can be adjusted.

REFERENCES

Gahler, A. R., Hamner, R. M., and Shubert, R. C., Anal. Chem. 33, 1937 (1961).

DETERMINATION OF MANGANESE IN NIOBIUM METAL
(PHOTOMETRIC WITH PERIODATE)

SCOPE

This procedure is designed for the determination of 1 to 100 p.p.m. of manganese in niobium metal.

PRINCIPLE OF METHOD

The metal is dissolved in HF and HNO₃, and the niobium cupferrate extracted with chloroform. After evaporation, the manganese is oxidized with periodate and determined photometrically as permanganate.

CONCENTRATION RANGE

The range of the method at 530 mμ using 5-cm. cells is 0 to 20 micrograms of manganese per 25 ml. The range can be extended up to 100 micrograms (0.1 mg.) of manganese per 25 ml. by preparing a suitable absorbance-concentration graph using 1-cm. cells. The colored system obeys Beer's law and is stable for at least 24 hours.

INTERFERENCES

There are no interferences from other metal ions in the concentrations normally found in niobium metal.

A slight turbidity due to niobium may be removed by centrifuging the colored solution just before photometric measurement.

SPECIAL REAGENTS

H₂SO₄ + H₃PO₄ Mixture - Mix 200 ml. of H₂SO₄ (1:1) and 100 ml. of 85% H₃PO₄. Dilute to 500 ml., heat to boiling, and cool.

Silver Nitrate (0.5 g./liter) - Dissolve 50 mg. of the salt in 100 ml. of water. Store in a brown glass dropping bottle.

Standard Manganese Solution - Dissolve 0.3476 g. of reagent grade KMnO₄ in 200 ml. of water, add 10 ml. of H₂SO₄ (1:1), and dilute to one liter. One ml. equals 0.1 mg. of manganese. Dilute a 10-ml. aliquot of this stock solution to 500 ml. One ml. equals 0.002 mg. (2 micrograms) of manganese.

SPECIAL APPARATUS

A spectrophotometer capable of utilizing 5-cm. cells.

SPECIAL PRECAUTIONS

All the glassware used in this determination must be thoroughly cleaned. The beakers should be boiled with nitric and perchloric acids, fumed strongly with perchloric acid, and thoroughly rinsed with distilled water. It is advisable to set aside glassware to be used exclusively for this determination. To obtain a low blank, it may be necessary to pass the distilled water through an ion-exchange column and store in a Pyrex bottle.

PREPARATION OF CALIBRATION GRAPH

Pipet 1-, 2-, 5-, 7-, and 10-ml. aliquots of the standard manganese solution (one ml. equals 2 micrograms of manganese) into 100-ml. beakers. Carry along a blank. Dilute to 10 ml., add 5 ml. of the H_2SO_4 - H_3PO_4 mixture and 3 drops of AgNO_3 solution. Add a Hengar (Al_2O_3) boiling chip, 0.050 g. of KIO_4 , cover, and boil gently for 10 minutes. Cool and transfer to a 25-ml. volumetric flask. Dilute to the mark and mix. Measure the absorbance at 530 m μ in 5-cm. cells using the blank as reference solution. Plot absorbance versus micrograms of manganese per 25 ml.

PROCEDURE

Carry a blank through the entire procedure.

Dissolve 1.000 g. of niobium metal in a 100-ml. platinum dish fitted with a platinum cover, using 5 ml. of HF and dropwise addition of HNO_3 . Add 10 ml. of H_2SO_4 and evaporate to light fumes of H_2SO_4 . Cool and add HF dropwise to obtain a clear solution. Transfer the sample to a polyethylene beaker containing 50 ml. of HF (2:98) solution. Rinse the platinum dish with HF (2:98) solution and add to the main solution. Chill the sample solution, the cupferron solution (saturated solution in water), and the chloroform to between 0 and 5°C. (Note 1).

Transfer the sample to a chilled, 250-ml. separatory funnel containing 50 ml. of the chilled cupferron suspension. Mix, add 100 ml. of the chilled chloroform and shake one minute. Withdraw the organic layer and discard. Add cupferron, about 5 ml. at a time until precipitation is complete. Repeat the extraction with 30 to 40 ml. of chloroform until the lower layer is colorless. Rinse the funnel stem with chloroform, then with water. Add 50 ml. of isopropyl ether and shake one minute.

Withdraw the aqueous layer to a 250-ml. Teflon beaker and evaporate to 50 ml. or less. Add 20 ml. of HCl and 10 ml. of HNO_3 , cover partially, and evaporate to remove ammonium salts and HF (Note 2). Cool, transfer to a 100-ml. Pyrex beaker. Add 4 or 5 drops of HClO_4 and again evaporate to one ml. of H_2SO_4 or less. Dilute to 10 ml. and neutralize with NaOH (pH paper). Continue as described in Preparation of Calibration Graph, starting with "Add 5 ml. of H_2SO_4 - H_3PO_4 mixture..." (Note 3).

NOTES

1. If the temperature of the solution is not less than 5°C., the niobium cupferrate is only slightly soluble. The cupferron solution should be freshly prepared, nearly colorless, and should contain some undissolved reagent.
2. If the solution turns black, add HNO_3 dropwise and repeat the fuming. Continue adding HNO_3 and evaporating to fumes until all organic matter is destroyed.
3. If the depth of color is beyond the range of 5-cm. cells, measure the absorbance in 1-cm. cells and refer to the proper calibration graph.

DETERMINATION OF MOLYBDENUM IN NIOBIUM METAL
(PHOTOMETRIC WITH THIOCYANATE)

SCOPE

This method is suitable for the determination of molybdenum in niobium within the range of 1 to 100 p.p.m.

PRINCIPLE OF METHOD

After dissolution of the sample in HF and HNO_3 and removal of the excess HF with H_2SO_4 , the niobium is complexed with ammonium citrate. The acidity is adjusted so that the H_2SO_4 concentration is 1:9. Ferric ion, sodium thiocyanate, and stannous chloride are then added. The molybdenum thiocyanate complex is extracted with butyl acetate and measured spectrophotometrically at 470 $\text{m}\mu$.

CONCENTRATION RANGE

The colored system follows Beer's law in the range from 1 to 25 micrograms of molybdenum in 30-ml. volume using 5-cm. cells. The range may be extended to 100 micrograms by using 1-cm. cells.

INTERFERENCES

Under the conditions of the method, a 100-to-1 ratio of other metals, besides molybdenum, which react with thiocyanate, is without measurable effect. Ferric ion is necessary for the molybdenum thiocyanate color system. However, if the final butyl acetate extract is contaminated with ferrous ion, the extract will have a pink tint instead of yellow. Thus, all glassware which will come in contact with the colored system after color development must be free from traces of iron. This will cause a positive error.

SPECIAL REAGENTS

Sodium Thiocyanate - Dissolve 20 g. of NaCNS in 100 ml. of water. Prepare fresh daily.

Stannous Chloride - Transfer 70 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ to a 250-ml. beaker. Add 20 ml. of concentrated HCl and warm until dissolved. Cool, transfer to a 200-ml. volumetric flask, and dilute to the mark. Add a small chunk of metallic tin as a preservative.

Ammonium Citrate - Dissolve 400 g. of ammonium citrate in one liter of water.

Sulfuric Acid Solution - Dilute 200 ml. of H_2SO_4 (1:1) to one liter, mix, and cool.

Butyl Acetate - Saturate the butyl acetate with a small excess of NaCNS and store in a dark bottle. Prepare fresh daily.

Ferric Sulfate Solution - Dissolve one gram of $\text{Fe}_2(\text{SO}_4)_3$ in 100 ml. of H_2SO_4 (1:9).

Standard Molybdenum Solution - Transfer 0.1800 g. of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (assay 83.0% MoO_3) to a 250-ml. beaker and dissolve in 50 ml. of H_2SO_4 (1:9) by warming. Transfer to a liter volumetric flask, cool, dilute to the mark, and mix. One ml. of this stock solution contains 0.1 mg. of molybdenum. Dilute 10.0 ml. of the stock solution to one liter with H_2SO_4 (1:99) (one ml. = one microgram of molybdenum).

PREPARATION OF ABSORBANCE-CONCENTRATION GRAPH

Transfer 0 (blank), 1-, 2-, 5-, 10-, and 25-ml. aliquots of the diluted molybdenum stock solution to 250-ml. beakers. Add 5 ml. of H_2SO_4 (1:9) and 2 ml. of ferric sulfate solution. Dilute to 50 ml. and chill in an ice bath to 4°C . or colder. Continue according to the procedure below, starting with "chill all reagents...." Measure the absorbance in 5-cm. cells at 470 $\text{m}\mu$ using the blank as reference solution. Plot absorbance versus micrograms of molybdenum on co-ordinate paper.

PROCEDURE

Transfer a one-gram sample to a 100-ml. platinum dish or 250-ml. Teflon beaker fitted with a cover. Add 10 ml. of HF and a few drops of HNO_3 to complete the dissolution. Add more HNO_3 and warm, if necessary. Add 10 ml. of H_2SO_4 and 2 ml. of formic acid, carefully swirl to mix, and evaporate until H_2SO_4 fumes begin to evolve (Note 1). Cool, add 10 ml. of ammonium citrate solution, stir, and transfer to a 250-ml. beaker. Polish the platinum dish and wash into the beaker. Adjust the pH of the sample solution to 5 to 7 (pH paper) with NH_4OH , dilute to 50 ml., and boil to obtain a clear solution. Add 10 ml. of H_2SO_4 (1:1) and 2 ml. of ferric sulfate solution (Notes 2 and 3).

Chill all reagents and the sample in an ice bath to 4°C . or colder. Transfer the sample to a 125-ml. separatory funnel by washing with 15 ml. of H_2SO_4 (1:9). Add 3 ml. of NaCNS solution and mix. Add 5 ml. of SnCl_2 solution, mix, and add exactly 30.0 ml. of butyl acetate. Shake vigorously for one minute and allow the phases to separate. Discard the lower layer. Add 50 ml. of H_2SO_4 (1:9), 2 ml. of NaCNS, and 2 ml. of SnCl_2 . Shake for one minute, separate, and discard the lower layer. Rinse the funnel stem with water and dry with a swab of filter paper.

Filter the butyl acetate layer through a small plug of cotton inserted in the funnel stem. Discard the first few ml. of the filtrate and collect the remainder in a dry, small flask. Measure the absorbance in a dry 5-cm. cell at 470 $\text{m}\mu$ using the blank as reference solution.

NOTES

1. Formic acid is added to decompose HNO_3 . Use care to avoid spray loss. Do not evaporate to dense fumes of H_2SO_4 . Add 1 or 2 drops of HF, if necessary, to clear the solution.

2. If the sample is known to contain more than 25 micrograms of molybdenum, dilute to volume and obtain a suitable size aliquot. Alternatively, the absorbance may be measured in 1-cm. cells if the concentration is not greater than 100 micrograms. In this case, prepare a calibration graph for the range 10 to 100 micrograms using 1-cm. cells.

DETERMINATION OF TANTALUM IN NIOBIUM
(PHOTOMETRIC WITH METHYL VIOLET)

SCOPE

This method is suitable for the determination of small amounts of tantalum (0.01 to 0.20%) in niobium.

PRINCIPLE OF METHOD

After dissolution of the sample, traces of boron are removed by volatilization with HF. The salts are fused in sodium bisulfate and the melt dissolved in ammonium oxalate solution. The tantalum is extracted as the methyl violet-fluoride complex into benzene and determined spectrophotometrically.

CONCENTRATION RANGE

The range using a 1-cm. cell is from 0.005 to 0.1 mg. of tantalum in 25 ml. of benzene. The colored system follows Beer's law and is stable for at least 4 hours in a stoppered container.

INTERFERENCES

Boron is a very serious interference and removal of boron by volatilization with HF is incorporated in the procedure (Note 1). Titanium, zirconium, and niobium do not interfere.

SPECIAL REAGENTS AND EQUIPMENT

Centrifuge

Centrifuge Tubes - 40-ml. volume, boron-free glass, quartz, or benzene-insoluble plastic tubes.

Methyl Violet - Dissolve 0.1 g. of methyl violet in 100 ml. of water.

Ammonium Oxalate - Dissolve 40 g. of ammonium oxalate in one liter of water.

Blank Solution - Fuse 8 g. of sodium bisulfate until sulfuric acid fumes are no longer evolved. Dissolve the melt in 100 ml. of ammonium oxalate and dilute to 200 ml. in a volumetric flask with water.

1.5N Hydrofluoric Acid - Dilute 27 ml. of 48% reagent-grade hydrofluoric acid to 500 ml. Store in a polyethylene bottle.

Standard Tantalum Solution - Dissolve 0.025 g. of tantalum metal or 0.0305 g. of tantalum pentoxide in 3 to 5 ml. of hydrofluoric acid to which 2 drops of nitric acid have been added. Add 2 ml. of H_2SO_4 and evaporate to dryness. Fuse with 4.0 g. of sodium bisulfate until sulfuric acid fumes cease to be evolved. Dissolve the melt in 50 ml. of ammonium oxalate (40 g./liter). Cool and transfer to a 100-ml. volumetric flask using water. Dilute to the mark with water. Each ml. is equal to 0.25 mg./ml.

Transfer a 10-ml. aliquot to a 50-ml. volumetric flask and dilute to the mark with the blank solution. Each ml. is equal to 0.050 mg./ml. Transfer a 10-ml. aliquot of this solution (0.050 mg. of tantalum per ml.) to a 50-ml. volumetric flask and dilute to the mark with the blank solution. Each ml. is equal to 0.010 mg./ml.

PREPARATION OF CALIBRATION GRAPH

Transfer aliquots containing 0.02, 0.05, 0.075, and 0.10 mg. of tantalum to 125-ml. separatory funnels. Carry along a blank at the same time. Dilute all the solutions by addition of sufficient quantity of the blank solution with a pipet to make up to 4 ml. (Note 2). Add 2 ml. of water. Working on each funnel separately, add the following reagents successively with pipets: 2.0 ml. of 1.5N hydrofluoric acid, 25.0 ml. of benzene, and 2.0 ml. of methyl violet. Shake exactly 20 seconds. Allow the layers to separate; immediately draw off the aqueous phase and discard. Immediately draw off the organic phase and store in a stoppered quartz centrifuge tube (Note 3). Complete the remaining aliquots in the same manner. Centrifuge for 20 to 30 seconds. Measure the absorbance of the benzene solution in a spectrophotometer in 1-cm. cells at 580 μ , nulling the instrument against the reagent blank. Plot absorbance versus milligrams of tantalum.

PROCEDURE

Transfer 0.500 g. of sample to a platinum dish. Add 10 ml. of hydrofluoric acid. Add nitric acid slowly and dropwise until the sample is dissolved. Add 2 ml. of sulfuric acid and evaporate to dryness on a sand bath to remove traces of boron (and silicon).

Cool, add 8.0 g. of NaHSO_4 , and fuse until sulfuric acid fumes cease to be evolved (Note 4). Dissolve the melt in 100 ml. of ammonium oxalate (40 g./liter). Cool and transfer to a 200-ml. volumetric flask using water. Dilute to the mark with water.

Start a blank by pipetting 20 ml. of the blank solution into a separatory funnel.

Transfer a 20-ml. aliquot to a separatory funnel and add 10 ml. of water. If more than one sample is being analyzed, handle each individually. Add 10 ml. of 1.5N hydrofluoric acid, pipet 25 ml. of benzene, and pipet 10 ml. of methyl violet solution. Shake vigorously for exactly 20 seconds. Allow the layers to separate, immediately draw off the aqueous phase and discard. Immediately draw off the organic phase and store in a stoppered quartz centrifuge tube. Complete the remaining samples in the same manner.

Centrifuge for 20 to 30 seconds. Measure the absorbance of the benzene solution in a spectrophotometer in 1-cm. cells at 580 μ , nulling the instrument against the reagent blank.

NOTES

1. Boron is the most serious of the interferences; however, it is not as sensitive as tantalum. Iodide, nitrate, and mercury (I) enhance the color. Calcium and rare earths inhibit the color formation slightly. Poluetkov, N. S., Kononenko, L. I., Lauer, R. S., Journal of Analytical Chemistry (U.S.S.R.) 13, 449 (1958) (English translation).

2. The pH for optimum extraction of the tantalum methyl violet-fluoride complex into benzene is 2.3. Careful additions are necessary to assure this pH.

3. If quartz or boron-free glass is unavailable, draw off and store the organic layer in a platinum or porcelain dish and cover with a watch glass. Handling each sample individually, transfer the organic layer to a centrifuge tube and centrifuge EXACTLY 20 seconds. Stop centrifuge as quickly as possible and measure the absorbance of the solution. Contact with glass must be held to a minimum because of the fluoride present which is necessary in the extraction.

4. Do not fuse for a prolonged time or the melt will not dissolve in the ammonium oxalate leach.

DETERMINATION OF TRACES OF TANTALUM IN NIOBIUM
(ION EXCHANGE SEPARATION AND PHOTOMETRIC
DETERMINATION WITH METHYL VIOLET)

SCOPE

This method is suitable for the determination of small amounts of tantalum (0.0005 to 0.20%) in niobium metal.

PRINCIPLE OF METHOD

The bulk of the niobium is separated on the ion exchange column containing Dowex 1 resin. The resin is decomposed by ignition, traces of boron are removed, if present, by volatilization with HF, the tantalum oxide is fused in NaHSO_4 , and the melt is dissolved in ammonium oxalate solution. The tantalum in an aliquot of the solution is extracted as the methyl violet-fluoride complex into benzene and determined spectrophotometrically.

CONCENTRATION RANGE

The range using a 1-cm. cell is from 0.01 to 0.1 mg. of tantalum in 25 ml. of benzene. The colored system follows Beer's law and is stable for at least 4 hours in a stoppered container.

INTERFERING ELEMENTS

Boron is a very serious interference and removal by volatilization with HF is incorporated in the procedure (Note 1). Titanium, zirconium, and niobium do not interfere (Note 4).

SPECIAL APPARATUS

1. The columns are constructed of transparent Tygon tubing, 12 inches long and 1/4 inch I.D. The flow is controlled by a hose cock on the Tygon tubing.

2. The resin is Dowex 1, 100 to 200 mesh, 8 to 10% divinylbenzene cross linkage. Prepare a suspension of the resin in dilute HCl (1:19).

3. A plug of Dynel wool, about 3/8 inch thick, is inserted into the tube about 2 inches from the bottom. Add the suspension of resin in one addition. Enough resin should be present to have a settled column about 4 inches high. Drain to just above the top of the column.

Ammonium Chloride-hydrofluoric Acid - Dissolve 140 g. of ammonium chloride and 40 ml. of hydrofluoric acid in water, and dilute to one liter with water. Store in a polyethylene bottle.

Hydrochloric Acid-hydrofluoric Acid - Add 250 ml. of HCl to 300 ml. of water, add 200 ml. of HF, and dilute to one liter with water. Store in a polyethylene bottle.

Centrifuge

Centrifuge Tubes - 40-ml. volume, boron-free glass, quartz, or benzene-insoluble plastic tubes.

Methyl Violet - Dissolve 0.1 g. of methyl violet in 100 ml. of water.

Ammonium Oxalate - Dissolve 40 g. of ammonium oxalate in one liter of water.

Blank Solution - Fuse 8 g. of sodium bisulfate until sulfuric acid fumes are no longer evolved. Dissolve the melt in 100 ml. of ammonium oxalate and dilute to 200 ml. in a volumetric flask with water.

1.5N Hydrofluoric Acid - Dilute 27 ml. of 48% reagent-grade hydrofluoric acid to 500 ml. Store in a polyethylene bottle.

Standard Tantalum Solution - Dissolve 0.025 g. of tantalum metal or 0.0305 g. of tantalum pentoxide in 3 to 5 ml. of hydrofluoric acid to which 2 drops of nitric acid have been added. Add 2 ml. of H_2SO_4 and evaporate to dryness. Fuse with 4.0 g. of sodium bisulfate until sulfuric acid fumes cease to be evolved. Dissolve the melt in 50 ml. of ammonium oxalate (40 g./liter). Cool and transfer to a 100-ml. volumetric flask using water. Dilute to the mark with water. Each ml. is equal to 0.25 mg./ml.

Transfer a 10-ml. aliquot to a 50-ml. volumetric flask and dilute to the mark with the blank solution. Each ml. is equal to 0.050 mg./ml. Transfer a 10-ml. aliquot of this solution (0.050 mg./ml.) to a 50-ml. volumetric flask and dilute to the mark with the blank solution. Each ml. is equal to 0.010 mg./ml.

PREPARATION OF CALIBRATION GRAPH

Transfer aliquots containing 0.02, 0.05, 0.075, and 0.10 mg. of tantalum to 125-ml. separatory funnels. Carry along a blank at the same time. Dilute all the solutions by addition of sufficient quantity of the blank solution with a pipet to make up to 4 ml. (Note 2). Add 2 ml. of water. Working on each funnel separately, add the following reagents successively with pipets: 2.0 ml. of 1.5N hydrofluoric acid, 25.0 ml. of benzene, and 2.0 ml. of methyl violet. Shake exactly 20 seconds. Allow the layers to separate; immediately draw off the aqueous phase and discard. Immediately draw off the organic phase and store in a stoppered quartz centrifuge tube (Note 3). Complete the remaining aliquots in the same manner. Centrifuge for 20 to 30 seconds. Measure the absorbance of the benzene solution in a spectrophotometer in 1-cm. cells at 580 $m\mu$ using the reagent blank to null the instrument. Plot absorbance versus milligrams of tantalum.

PROCEDURE

Transfer a suitable sample (1.00 to 5.00 g.) to a 300-ml. platinum dish. Add 10 ml. of hydrofluoric acid and nitric acid dropwise until the sample is dissolved. Evaporate on a steam bath until almost dry. The bottom of the dish should still be moist. Add 50 ml. of the ammonium chloride-hydrofluoric acid solution and warm gently to obtain a clear solution.

Cool, transfer the solution to the column in small increments, and drain to 1 cm. above the resin bed. Add 25 ml. of the hydrochloric-hydrofluoric acid in

small increments and allow to drain dry. Transfer the resin and Dynel plug to a 100-ml. platinum dish with a jet of water. Evaporate on a sand bath until dry. Ignite at a low temperature and finally at 500°C. to remove all organic matter.

Cool and add 5 ml. of hydrofluoric acid and 2 ml. of H_2SO_4 , and heat on a sand bath to dryness to remove traces of boron (and silicon).

Cool, add 4.0 g. of NaHSO_4 and fuse until sulfuric acid fumes cease to be evolved. Dissolve the melt in 50 ml. of ammonium oxalate (40 g./liter). Cool and transfer to a 100-ml. volumetric flask using water. Dilute to the mark with water.

Transfer a 20-ml. aliquot to a separatory funnel. Transfer a 20-ml. aliquot of the blank solution to a separatory funnel. Add 10 ml. of water. Proceed on each funnel separately. Add the following reagent successively with pipets: 10.0 ml. of 1.5N hydrofluoric acid, 25.0 ml. of benzene, and 10.0 ml. of methyl violet. Shake exactly 20 seconds. Allow the layers to separate; immediately draw off the aqueous phase and discard. Immediately draw off the organic phase and store in a stoppered quartz centrifuge tube (Note 3). Complete the remaining aliquots in the same manner. Centrifuge for 20 to 30 seconds. Measure the absorbance of the benzene solution in a spectrophotometer in 1-cm. cells at 580 m μ using the reagent blank to null the instrument. Find the concentration of tantalum present in the aliquot by reference to the calibration graph.

NOTES

1. Boron is the most serious of the interferences; however, it is not as sensitive as tantalum. Iodide, nitrate, and mercury (I) enhance the color. Calcium and rare earths inhibit the color formation slightly. N. S. Poluetkov, L. I. Kononenko, R. S. Lauer, JOURNAL OF ANALYTICAL CHEMISTRY (U.S.S.R.) 13, 449 (1958) (English translation).

2. The pH for optimum extraction of the tantalum methyl violet-fluoride complex into benzene is 2.3. Careful additions are necessary to assure this pH.

3. If quartz or boron-free glass is unavailable, draw off and store the organic layer in a platinum or porcelain dish and cover with a watch glass. Handling each sample individually, transfer the organic layer to a centrifuge tube and centrifuge EXACTLY 20 seconds. Stop centrifuge as quickly as possible and measure the absorbance of the solution. Contact with glass must be held to a minimum because of the fluoride present which is necessary in the extraction. If boron-free equipment is used, the timing of extraction and centrifuging is not critical.

4. To reduce boron contamination, reserve a set of equipment for use with this determination only.

DETERMINATION OF SMALL AMOUNTS OF TIN IN NIOBIUM METAL
(PHOTOMETRIC WITH PYROCATECHOL VIOLET)

SCOPE

This method is designed for the determination of tin in niobium in the range of 0.0003 to 0.5%.

PRINCIPLE OF METHOD

The sample is dissolved in HF and HNO₃ acids. After removal of HF and HNO₃ by fuming with H₂SO₄, the final solution is adjusted to approximately 1M in HCl and 2M in H₂SO₄. The tin (IV) is extracted with 0.01M tris(2-ethylhexyl)-phosphine oxide in cyclohexane. Any interfering ions such as antimony or arsenic are removed by back-extraction with a 1M HCl-2M H₂SO₄ mixture. The color is developed with pyrocatechol violet and measured spectrophotometrically at 575 mμ.

CONCENTRATION RANGE

The colored system follows Beer's law over the range of 3 to 30 micrograms of tin in 10 ml. of organic solvent using 1-cm. cells. The colored system is stable for at least 12 hours.

INTERFERENCES

Antimony, arsenic, and chromium (VI) interfere with the colored system but these elements are not ordinarily found in high-purity niobium metal, and chromium remains as chromium (III) in the steps of the procedure. HF and HNO₃ interfere but are removed by volatilization by strong fuming with H₂SO₄.

REAGENTS AND SOLUTIONS

Standard Tin Solution - Dissolve 0.1000 gram of tin in 100 ml. of HCl. Cool and dilute to one liter with water. Pipet 10.0 ml. of this solution to a 100-ml. volumetric flask. Dilute to volume with the 1M HCl-2M H₂SO₄ mixture. Each ml. contains 10 μg. (micrograms) of tin.

1M HCl-2M H₂SO₄ Mix - Add 85 ml. of concentrated HCl to 222 ml. of H₂SO₄ (1:1), and dilute to one liter with water.

Tris(2-Ethylhexyl)Phosphine Oxide Solution (TEHPO) - 0.01M in cyclohexane (3.8665 g./liter): The reagent is available from Chemicals Procurement Company, 18-17 130th Street, College Point, Long Island, or K & K Laboratories, Inc., 177-10 93rd Avenue, Jamaica 33, New York.

Pyrocatechol Violet (0.5 g./liter) - Weigh out 0.0500 g. of pyrocatechol violet in a 100-ml. volumetric flask. Dilute to volume with 95% ethanol. Shake until dissolved. Prepare FRESH daily.

Pyridine - Reagent grade.

PREPARATION OF CALIBRATION GRAPH

Pipet 0 (reagent blank), 1-, 2-, 5-, and 10-ml. portions of the standard tin solution into clean, dry 125-ml. separatory funnels. Add 5 ml. of the TEHPO solution with a pipet and shake for 10 minutes. Allow the layers to separate, drain off the aqueous portion and discard. Pipet 2.0-ml. portions of the organic phase into clean, dry 10-ml. volumetric flasks. Add 2.0 ml. of the pyrocatechol violet solution with a pipet into each flask and mix. Pipet 1.0 ml. of pyridine into each volumetric flask and mix. Dilute to volume with 95% ethanol and mix well. Allow to stand in a water bath (55 to 65°C.) for 20 minutes. Cool to room temperature.

Measure the absorbance of the solution in 1-cm. cells at maximum absorbance which occurs near 575 m μ , placing the reagent blank in the reference cell.

Prepare the absorbance-concentration graph by plotting the absorbance of the solutions versus tin concentration.

PROCEDURE

Dissolve the sample in HF with dropwise addition of HNO₃ in a platinum dish (Note 1). Carry a blank through all steps of the procedure. Add 22 ml. of H₂SO₄ (1:1) and evaporate to strong fumes of sulfuric acid. Wash down the sides of the dish with water and evaporate to strong fumes. Repeat once again. Cool, add 25 ml. of water, and warm on the hot plate. Transfer the sample to a 100-ml. volumetric flask containing 9.0 ml. of HCl. Cool to room temperature, dilute to volume, shake well, and allow to stand until the bulk of hydrolyzed niobium settles to the bottom. Filter 60 to 65 ml. of the solution through a Whatman filter No. 40 paper or equivalent into a clean beaker. (Some of the hydrolyzed niobium will run through the paper, but will be removed later in the procedure.) Transfer an aliquot containing 5 to 75 μ g. of tin to a clean, dry separatory funnel. Add 5.0 ml. of the TEHPO solution with a pipet and shake for ten minutes. Allow the layers to separate, draw off the aqueous portion, and discard. Add 5 ml. of 1M HCl-2M H₂SO₄ solution, and shake again for five minutes. Draw off the aqueous portion and discard. The hydrolyzed niobium will form an emulsion with the organic. Transfer to a centrifuge and centrifuge for a minute or two. Draw off a 2-ml. portion of the organic phase with a pipet and proceed as outlined under Preparation of Calibration Graph.

NOTES

1. If the sample contains acid-insoluble tin, such as oxide, the solution, after acid dissolution, may be filtered and the residue burned off at 600°C. in a porcelain crucible. The residue is then fused with a known weight of Na₂CO₃ and dissolved in the acid solution. A blank must be carried through all steps of this procedure. Any tin compound infusible in Na₂CO₃ cannot be run with this method since ordinary Na₂O₂ contains too much tin as an impurity.

REFERENCES

1. Ross and White, Anal. Chem. 33, 421 (1961)
2. Ibid., 33, 424 (1961)

DETERMINATION OF TUNGSTEN IN NIOBIUM
(SPECTROPHOTOMETRIC WITH DITHIOL)

SCOPE

This method is applicable for the determination of tungsten in niobium greater than 5 p.p.m. By suitable modification, tungsten can be determined down to 1 p.p.m. (Note 4).

PRINCIPLE OF METHOD

The sample is dissolved in HF and HNO₃, and then fumed gently in H₂SO₄ to remove the HNO₃. Molybdenum is separated by extraction from an HCl (1:4) solution with dithiol in amyl acetate. Tungsten is reduced in 9 to 11N HCl with Ti(III), extracted with dithiol, and determined spectrophotometrically.

CONCENTRATION RANGE

The range extends from 0.005 to 0.20 mg. of tungsten in 25 ml. of amyl acetate using 1-cm. cells if the absorbance is measured at 640 mμ (Note 4).

INTERFERENCES

There are no interferences from other metal ions in the concentrations normally found in niobium metal. However, if appreciable molybdenum is present, this method is not applicable (Note 1).

SPECIAL REAGENTS AND SOLUTIONS

Zinc Dithiol Solution - Dissolve 1.0 g. of zinc dithiol in 100 ml. of NaOH (10 g./liter) solution. Prepare just before use. The zinc dithiol is available from Fisher Scientific Company.

Isoamyl Acetate - Purified grade. The liquid should be colorless.

Tin (II) Chloride Solution - Dissolve 200 g. of SnCl₂·2H₂O in 500 ml. of HCl and dilute to one liter with water. Place a few pieces of metallic tin in the solution.

Titanium (III) Chloride Solution - Dissolve 10 g. of tungsten-free titanium metal with 200 ml. of HCl (1:1) in an Erlenmeyer flask. As soon as the metal has dissolved, cool the solution, dilute to 500 ml. with HCl (1:1), and store in a stoppered bottle.

Dithiol (Toluene-3,4-dithiol) - Obtainable in one-gram vials from Eastern Chemical Corp., 24 Spring Street, Newark, New Jersey. The reagent should be kept refrigerated until needed, and, if possible, under an inert atmosphere (Note 2).

Standard Tungsten Stock Solution (100 micrograms per ml.) - Dissolve 0.1794 g. of Na₂WO₄·2H₂O in water. Add 100 ml. of sodium hydroxide solution (100 g./liter) and dilute to one liter. Store in a caustic-resistant bottle.

Dilute Standard Tungsten Solution (10 micrograms per ml.) - Dilute 50 ml. of the standard tungsten stock solution (100 micrograms per ml.) to 500 ml. with water.

PREPARATION OF CALIBRATION GRAPH

Transfer 0 (blank), 1-, 2-, 5-, 10-, 15-, and 20-ml. aliquots of the dilute standard tungsten solution (10 μ /ml.) to a 125-ml. flask. Add 3 ml. of sulfuric acid and evaporate to light fumes of sulfuric acid. Cool. Cautiously add 5 ml. of water, 25 ml. of HCl, 5 ml. of tin (II) chloride solution, and 10 ml. of titanium (III) chloride solution (Note 2). Heat to about 80 to 90°C. and add 10 ml. of zinc dithiol solution. Heat in a hot water bath at 80 to 90°C. for 20 minutes. Cool and transfer to a separatory funnel, rinse with two 5-ml. portions of HCl (4:1). Add 25.0 ml. of isoamyl acetate with a pipet and shake vigorously for one minute. Allow the layers to separate, draw off the aqueous phase and discard. Wash the organic layer twice with 3-ml. portions of HCl (4:1). Discard the acid washings.

Transfer a portion of the colored organic solution to 1-cm. cells. Measure the absorbance of the solution at 640 m μ versus the blank which is placed in the reference cell of the spectrophotometer. Prepare a calibration graph by plotting concentration versus absorbance of the solution. The colored system follows Beer's law and is stable for 24 hours (Note 3).

PROCEDURE

Transfer a sample not greater than one gram or containing not more than 0.2 mg. of tungsten to a 50-ml. platinum dish. Add 5 ml. of HF and HNO₃ dropwise until the sample is in solution. Add 3 ml. of H₂SO₄ and evaporate to light fumes. Cool and add 0.5 ml. of HF.

Add 15 ml. of HCl (1:4). Transfer to a 125-ml. Erlenmeyer flask and use 5 ml. of HCl (1:4) to rinse the platinum dish. Cool to below 10°C. and add 5 ml. of tin (II) chloride. Add 10 ml. of dithiol amyl acetate solution (0.5 g. of dithiol (not zinc dithiol) per 100 ml. of amyl acetate), cork with a rubber stopper, and shake 5 minutes on a mechanical shaker. Transfer to a separatory funnel and rinse the flask with two 5-ml. portions of amyl acetate. Allow the layers to separate. Transfer the acid layer containing the tungsten quantitatively back to the Erlenmeyer flask. (Discard the amyl acetate layer which contains the molybdenum.) Evaporate to fumes of sulfuric acid. If charring occurs, add several drops of HNO₃, and again evaporate to fumes of sulfuric acid. Cool, add 0.5 ml. of HF, and cautiously add 40 ml. of HCl. Continue as in the Preparation of Calibration Graph, starting with "Add 5 ml. of tin (II) chloride solution, add 10 ml. of titanium (III)...."

NOTES

1. About 0.4 mg. of molybdenum may be removed by extraction in the procedure. The method is not applicable if more than this concentration is present in the sample or aliquot.
2. The acidity of the solution must be between 9 and 11N for complete reduction of tungsten (VI) to tungsten (V).
3. If the organic layer is turbid, it can be filtered through a cotton plug.
4. The range can be lowered by measuring the absorbance in 5-cm. cells.

DETERMINATION OF TRACES OF ZIRCONIUM AND TITANIUM IN NIOBIUM
(ION EXCHANGE-SPECTROPHOTOMETRIC METHOD)

SCOPE

This method is designed for the determination of traces (p.p.m.) of zirconium and titanium in niobium metal. The same procedure is applicable for these elements in tantalum metal.

PRINCIPLE OF METHOD

After dissolution of the sample in HF and HNO₃ acids and removal of the nitric acid, the solution is adjusted to HF (1:9) and HCl (1:1). The solution is passed through an ion exchange column containing Dowex 1 anion resin. Zirconium and titanium pass through the column while tantalum and niobium remain on the column. Zirconium is determined spectrophotometrically with phenylfluorone. The titanium is extracted as the thiocyanate complex by tri-n-octylphosphine oxide (TOPO) dissolved in cyclohexane and is determined spectrophotometrically.

CONCENTRATION RANGE

The concentration range for zirconium extends from 1 to 4 micrograms (μg.) in 25 ml. using 5-cm. cells. The system follows Beer's law and is stable for 3 hours.

The concentration range for titanium extends from 1 to 5 micrograms (μg.) in a volume of 25 ml. using 1-cm. cells. The system follows Beer's law and is stable for 12 hours.

INTERFERENCES

Zirconium - Alkali metals, alkaline earths, thorium, aluminum, zinc, cadmium, and bivalent metals do not interfere. Titanium, tin, colored ions, antimony, tantalum, niobium, hafnium, phosphate, fluoride, and nitrate interfere, as well as excessive amounts of sulfate. Interference of iron, chromium, cobalt, nickel, bismuth, silver, tungsten, niobium, and tantalum is eliminated by the ion exchange separation. The small amount of titanium remaining is eliminated by an H₂O₂-ammonium hydroxide separation. Nitrate, fluoride, and excessive amounts of sulfate are eliminated by volatilization when fuming down almost to dryness before the color development.

Titanium - Niobium interferes by formation of a color. Niobium interference is eliminated by the ion exchange separation.

APPARATUS AND RESIN

1. ION EXCHANGE COLUMNS

The columns are constructed of polystyrene and are approximately 18 inches long and one inch I.D. The bottom of the tube is closed by a waxed No. 5 rubber stopper with a 3/16-inch hole. A 3-inch length of polystyrene tubing with a 3/16 inch O.D. is inserted in the hole. A 3-inch length of Tygon tubing is attached and the flow controlled by a hose cock on the Tygon tubing.

2. RESIN

The column packing is Dowex 1 resin, 200 to 400 mesh, 8 to 10% divinylbenzene cross linkage. Prepare a suspension of the resin in dilute HCl (1:19). Allow the coarser fraction to settle 10 to 15 minutes and remove the fines by decantation. Repeat the process about 7 to 8 times until most of the fine material is removed from the suspension.

3. PREPARATION OF COLUMN

The bottom of the ion exchange column is covered with a 1/4- to 3/8-inch layer of acid-resistant vinyl chloride plastic wool (Dynel). Transfer the suspension of resin to the column in one addition. Sufficient resin should be present to form a settled column 12 inches high. The loaded column should be eluted several times alternately with HCl (3:1) and HCl (1:9) to remove the fines. The column is then washed with HCl (1:3) and is ready for use. At no time should the column be allowed to run dry. The flow rate should be about 100 to 125 ml. per hour.

4. POLYETHYLENE WARE

400-, 600-, and 1000-ml. beakers and bottles for preparing, storing, and dispensing acid mixtures. Graduated 100-ml. cylinder.

SOLUTIONS AND REAGENTS

Hydrochloric-hydrofluoric Acid Solution - Add 100 ml. of HF to 200 ml. of water, add 500 ml. of HCl, and dilute to one liter with water. Cool to room temperature.

Ammonium Chloride Solution (240 g./liter) - Dissolve 240 g. of NH_4Cl in 800 ml. of water, and dilute to one liter with water.

Niobium and Tantalum Eluant - To 600 ml. of the ammonium chloride solution, add 40 ml. of HF. Adjust the pH from 5.5 to 6.5 with NH_4OH . (Approximately 80 to 85 ml. will be required.) Dilute to one liter with water (Note 1).

Gelatin Solution (5 g./liter) - Dissolve 0.5 g. of gelatin in 100 ml. of boiling water.

Phenylfluorone (0.3 g./liter) - 0.0300 g. of phenylfluorone in 100 ml. of ethanol containing one ml. of HCl. Mix on a shaker until clear. The solution is stable for one week.

Zirconium Standard Solutions

A. Stock Solution - Dissolve 0.0353 g. of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 50 ml. of HCl and dilute to one liter.

B. Dilute Standard Solution - Pipet a 10-ml. portion of the stock solution into a 200-ml. volumetric flask, add 25 ml. of HCl, and dilute to volume. Each ml. contains 0.5 microgram ($\mu\text{g.}$) of zirconium and 0.25 ml. of HCl.

Titanium Standard Solutions

A. Stock Solution - Dissolve 0.0500 g. of titanium metal in 100 ml. of HCl. Transfer to a liter volumetric flask, add 400 ml. of HCl, and dilute to volume with water. (Solution is $6N$ or (1:1) with respect to HCl.)

B. Dilute Standard Solution - Pipet a 5-ml. portion of the stock solution to a 500-ml. volumetric flask, add 250 ml. of HCl, and dilute to volume with water. Each ml. contains 0.5 microgram ($\mu\text{g.}$) of titanium. The HCl concentration is about $6N$ or (1:1).

Tri-n-octylphosphine Oxide Solution (TOPO) - Approximately 0.01M in cyclohexane. Dissolve 3.9 g. of tri-n-octylphosphine oxide (Eastman Chemical Products, Inc., Eastman Kodak Company) in one liter of cyclohexane.

PREPARATION OF ZIRCONIUM CALIBRATION GRAPH

Transfer 0 (blank), 1-, 2-, 4-, 6-, and 8-ml. aliquots of the dilute standard zirconium solution to 25-ml. volumetric flasks. Add enough HCl (1:1) to each flask to contain one ml. of concentrated HCl per 25 ml. volume. Dilute to about 10 ml. with water, add 2 ml. of gelatin solution, 5 ml. of phenylfluorone solution, dilute to volume, mix well, and allow to stand for 30 minutes. Measure the absorbance of the solution versus the blank in 5-cm. cells at maximum absorbance which occurs near 535 $m\mu$.

Prepare the absorbance-concentration graph by plotting the absorbance of the solution versus the zirconium concentration.

PREPARATION OF TITANIUM CALIBRATION GRAPH

Transfer 2-, 4-, 6-, 8-, and 10-ml. aliquots of the dilute standard titanium solution to 125-ml. separatory funnels. Add 150 mg. of solid sodium thiocyanate per ml. of solution. The resulting mixture is extracted for 5 minutes on a shaker with 5 ml. of the TOPO solution. A reference solution which contains the reagents but no titanium is similarly extracted to use as a blank. Draw off the aqueous phase and discard. Dry the funnel stem with a swab of filter paper. Place a glass wool plug in the stem of the separatory funnel and fill a 1-cm. cell with the organic solution. Measure the absorbance of the solution at maximum absorbance which occurs near 432 $m\mu$ versus the reference solution. Clean the separatory funnels with ethanol, water, nitric acid, and a thorough washing with water, in that order.

Prepare the absorbance-concentration graph by plotting the absorbance of the solutions versus the titanium concentration.

PROCEDURE

Carry a reagent blank through all steps of the procedure. To a sample containing 1 to 10 $\mu\text{g.}$ of zirconium and/or 1 to 10 $\mu\text{g.}$ of titanium in a large platinum dish, add HF and dropwise addition of HNO_3 . Evaporate on a steam bath until almost dry. Add 10 ml. of HF, 1 ml. of formic acid, and evaporate until almost dry again (Notes 2 and 3). Add 50 ml. of the HCl-HF solution and warm gently to obtain a clear solution. Adjust the column to the proper acid condition by transferring 75 ml. of the HCl-HF solution to the column in small increments

(5 to 10 ml.) and drain the acid to 1 cm. above the resin bed. Discard the liquid which runs through. Place a clean 600-ml. polyethylene beaker under the column.

Cool the sample and transfer to the column in small increments (5 to 10 ml.). Wash the platinum dish 4 to 5 times with 5-ml. portions of the HCl-HF solution, transferring the washings to the column. Wash down the sides of the column several times using approximately 25 ml. of the HCl-HF solution. Drain to one ml. above the resin bed, collecting the eluate in the 600-ml. polyethylene beaker.

Keep the same beaker under the column and add 300 ml. of the HF-HCl solution at a flow rate of 100 to 125 ml. per hour. Allow the solution to drain to the top of the resin. The solution in the beaker contains the titanium and zirconium.

Clean up the column for the next sample by flowing 450 ml. of the niobium-tantalum eluant through the column at the same flow rate to remove the niobium and tantalum (Note 4).

Add 10 ml. of H_2SO_4 (1:1) to the solution containing the titanium and zirconium in the polyethylene beaker. Transfer the solution to a platinum dish and evaporate down to strong fumes of sulfuric acid. Any organic present is destroyed by dropwise addition of HNO_3 and by evaporation to strong fumes of sulfuric acid again. Cool, add 20 ml. of water, and mix well. Transfer the solution into a 100-ml. volumetric flask containing 50 ml. of HCl. Cool and dilute to volume with water.

To determine titanium, transfer an aliquot (up to 25 ml.) to a 125-ml. separatory funnel and proceed as outlined under Preparation of Titanium Calibration Graph. Measure the absorbance and determine the concentration of titanium by reference to the calibration graph.

To determine zirconium, transfer a 50-ml. aliquot to a 150-ml. beaker and evaporate to fumes of H_2SO_4 . Cool, add 50 ml. of water, 5 ml. of H_2O_2 (30%) and about 10 ml. of an aluminum chloride solution (1 g./liter), and make just ammoniacal to pH paper. Heat this solution to boiling and filter through a 9-cm. Whatman No. 40 or equivalent filter paper, washing 10 times with hot NH_4Cl solution (20 g./liter) containing 5 ml. of H_2O_2 (30%) per 100 ml. of solution. Place the paper back in the beaker, add 50 ml. of HNO_3 , 3 ml. of $HClO_4$, and 2 ml. of H_2SO_4 (1:1). Evaporate to fumes of $HClO_4$, cool, wash down the cover and beaker with water, and add 1 ml. of formic acid. Evaporate almost to dryness on the hot plate. (Less than 0.5 ml. of H_2SO_4 remains.) Cool, add 2 ml. of HCl solution (1:1) and 5 to 10 ml. of water, heat to dissolve salts, and cool. Transfer the solution to a 25-ml. volumetric flask and proceed as outlined under Preparation of Zirconium Calibration Graph, beginning with "Add two ml. of gelatin solution...." Measure the absorbance and determine the concentration of zirconium by reference to the calibration graph.

NOTES

1. This solution should be prepared with care. If the solution is too acid, tantalum will not be completely eluted in the volume specified. If the eluant is too alkaline, tantalum will precipitate in the column spoiling the determination being run and the one to follow.

2. If acid-insoluble zirconium, probably ZrO_2 , is suspected of being present, the solution is evaporated to dryness at this point and the residue fused with potassium pyrosulfate. The melt is then dissolved in the HCl-HF mixture and the rest of the procedure is followed as outlined.

3. It is necessary that all traces of nitric acid are removed before passing the solution through the column. Formic acid decomposes the nitric acid.

4. Periodically the column must be repacked because of changes in the physical form of the column. Channeling occurs after frequent use and niobium begins to appear in the eluate. When this occurs, the resin should be removed from the column, reslurried, and returned to the column.

REFERENCE

Young, J. P., and White, J. C., "Extraction of Titanium Thiocyanate with Tri-n-Octylphosphine Oxide," Anal. Chem. 31, 393 (1959).

APPENDIX II - EMISSION SPECTROGRAPHIC METHODS FOR TRACE ELEMENTS IN NIOBIUM METAL

DETERMINATION OF ALUMINUM IN NIOBIUM METAL OR OXIDE (EMISSION SPECTROGRAPHIC METHOD)

SCOPE

This procedure is designed for the determination of 3 to 100 p.p.m. of aluminum in niobium metal or oxide.

PRINCIPLE OF METHOD

The oxide sample is mixed with graphite and analyzed using an AC arc, double cap mix technique.

APPARATUS

Any commercial spectrograph with a dispersion of 6A/mm. and a direct-current excitation source is believed suitable for the determination. This procedure refers to the equipment listed below.

Spectrographic Apparatus

3-meter grating spectrograph	Baird Model AD-1
Source unit	Baird Model AK-3
Densitometer	Baird Model CD
Boron carbide mortar	
Pelleting press with 1/8-inch die	

SPECIAL MATERIALS

Aluminum Standard Solutions (one mg./ml. and 0.02 mg./ml.) - Prepare a standard solution containing one mg./ml. of aluminum. Dissolve 0.500 g. of high-purity aluminum metal using a mixture of one part HCl, one part HNO₃, and four parts water, and dilute to 500 ml. Before use, dilute one ml. of this mixture to 50 ml. using high-purity redistilled water to make the 0.02 mg./ml. solution.

PROCEDURE

A. PREPARATION OF THE SAMPLE

Place the finely-divided metal in a platinum or silica flat dish, and heat in a muffle furnace for one hour at 700 to 800°C. Select a portion of the converted oxide and grind in a large boron carbide mortar to obtain a representative sample. Because of the abrasive qualities of Nb₂O₅ and the critical nature of the aluminum determination, all samples and standards are hand-ground, although power-driven facilities exist.

Grind equal weights (70 mg.) of representative oxide and SP-1 graphite pelleting powder in a small boron carbide mortar. High-purity 1/8-inch spectroscopic graphite rod is notched with a sharp knife and broken into 3/16-inch lengths.* A scoopful of the oxide-graphite mix (about 18 milligrams) is pelleted on the rough fractured end of the graphite rod. The capped electrode is inserted in the end of

*Actually 3/8-inch cut lengths are broken in half.

a length of 1/4-inch diameter graphite rod containing a slightly tapered 1/8-inch diameter hole.

For each arcing, two vertically opposed pellets are used. In aligning the electrode gap, provision is made for the cap mix to expand after the arc is started. A 3-mm. starting gap results in about a 2-mm. gap.

B. PREPARATION OF STANDARDS

A suitable source of low-aluminum Nb_2O_5 is salted using the aluminum standard solution. A 100-p.p.m. standard is prepared as follows. Two grams of oxide are placed in a small platinum fusion crucible and 0.2 ml. of one mg./ml. aluminum standard solution are pipetted onto the Nb_2O_5 , care being taken to avoid wetting the sides of the platinum crucible. After the contents of the crucible have been dried on a sand bath or asbestos-covered hot plate, the crucible is heated in a muffle furnace for one-half hour at 800°C. The contents are then hand-ground in a large boron carbide mortar using a preliminary wet grind with acetone.

Standards of lower aluminum content are prepared by dilution of the 100-p.p.m. standard with Nb_2O_5 . For example, 3 parts of Nb_2O_5 are dry-ground with one part of 100-p.p.m. standard to make the 25-p.p.m. standard. Alternately standards are also prepared by salting batches of Nb_2O_5 with the 0.02 mg./ml. standard solution.

When the working curves are plotted, a correction is made for the residual aluminum content using the method of straight line approximation.

SPECTROGRAPHIC CONDITIONS

Spectrograph	Baird 3-meter
Setting	First order 2600 to 4100 Å
Slit	25 micron
Lens	25-cm. focused on the grating
Grating	10-mm. exposure
Sector	Three step 1:2 ratio
Excitation	AC arc, 2700 volts and 4.5 amperes
Analytical gap	2-mm. while arcing
Upper electrode	Cap mix electrode
Lower electrode	Cap mix electrode
Exposure	25 seconds, no preburn
Emulsion	Spectrum Analysis #1
Development	3 minutes in D-19 at 70°F. $\pm 1^\circ$
Calibration	"Two Iron Line" method for 2500 to 3200 Å region. Step sector method for 3900 to 4000 Å region.

Lines used

<u>Al 3961</u>	1st, 2nd, or 3rd step - background corrected
Nb 3970	Step 3, no background correction

<u>Al 3082</u>	Step 2, background on high wave length
Nb 3106.9	Step 3, no background

4. Polyethylene Water - 400-, 600-, and 1000-ml. beakers and bottles for preparing and dispensing acid mixtures.

REAGENTS

Hydrochloric-hydrofluoric Acid Solution - Add 250 ml. of HCl to 300 ml. of water, add 200 ml. of HF, and dilute to one liter with water.

Standard Ammonium Chloride Solution - Dissolve 240 g. of NH_4Cl in 800 ml. of water and dilute to one liter with water.

Titanium, Tin, Vanadium, and Zirconium Eluant - To 300 ml. of the ammonium chloride solution, add 200 ml. of HF and 125 ml. of HCl, and dilute to one liter with water.

Niobium and Tantalum Eluant - To 600 ml. of the ammonium chloride solution, add 40 ml. of HF. Adjust the pH to 5.5 to 6.5 with NH_4OH . (Approximately 80 to 85 ml. will be required). Dilute to one liter with water (Note 1).

SPECTROGRAPHIC APPARATUS

Any commercial spectrograph with a dispersion of 6 A./mm. and a direct-current excitation source is believed suitable for this determination. This procedure refers to the equipment listed below.

Spectrographic Apparatus

3-meter grating spectrograph	Baird Model AD-1
Source unit	Baird Model AK-3
Densitometer	Baird Model CB
Boron carbide hand mortar	

SPECIAL MATERIALS FOR SPECTROGRAPHIC ANALYSIS

Graphite Containing 1% GeO_2 and 0.25% PdCl_2 - Prepare by dry-grinding in a mechanical mortar a mixture of 900 mg. of high-purity SP-1 briquetting graphite and 100 mg. of $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ (Fisher Scientific). In the same manner, prepare a 10% GeO_2 in graphite mixture. Dilute these and blend succeeding mixtures with graphite to make a concentration of 1% GeO_2 and 0.25% PdCl_2 . At no time is a greater dilution than 1:9 employed.

PREPARATION OF EMISSION SPECTROGRAPHIC STANDARDS

Standards are prepared by dry-grinding oxides of the elements with suitably pure tantalum oxide. Often two or more sets of standards containing the same but different combinations of other elements are available for cross checking. Where chemical concentration techniques are employed, additional standards are prepared using similar chemical procedures. For example, oxides may be prepared from cupferron precipitates of salted solutions or may be derived from salted solutions carried through the entire concentration operation.

PROCEDURE

A. PREPARATION OF SAMPLE

Place the finely divided metal in a platinum or silica flat dish and heat in a muffle furnace for one hour at 700 to 800°C. Select a portion of the converted oxide and grind in the agate mortar to obtain a representative sample. Nb_2O_5 samples of chemical origin are also preground to obtain a representative sample. Two-hundred mg. of the representative sample are then ground with 30 mg. of gallium oxide containing 1% As_2O_3 . Generally the small amount of gallium oxide is initially mixed with the Nb_2O_5 by hand in the mechanical mortar and then the power is turned on. The sample is ground for 15 to 20 minutes with frequent scraping down of the sides and pestle. A fine particle size is desirable for good precision and also to obtain similarity between coarse oxides obtained directly from metal and fine oxides of chemical origin.

Fifty mg. of the niobium oxide-gallium oxide mixture are weighed into a National electrode Type L4024. The mixture is loaded in three additions. A weighing glass with a 1/8-inch hole in the center or similarly shaped piece of metal containing a small hole in one end is helpful in loading the electrode. After each addition the electrode is held with forceps and tapped firmly and forcibly against the table top to ensure dense packing inside the electrode. The tapping operation cannot be overdone and should last for 30 seconds or more. When loaded, the electrode is inverted and the packed charge remains firmly in place. (A small speck of coarse grain is disregarded; also the air vent hole employed by some workers on U_3O_8 is not used.) Duplicate samples are normally employed in the analysis.

B. PREPARATION OF STANDARDS

A suitable source of low-boron Nb_2O_5 is salted using the boron standard solution. A 10-p.p.m. standard is prepared as follows: 2 grams of oxide are placed in a small platinum fusion crucible and 0.1 ml. of 0.2 mg./ml. boron standard solution is added to the oxide without wetting the sides of the dish. The platinum dish is gently dried on a sand bath or drying oven and then placed in a muffle furnace for one hour at 600°C. After cooling, the oxide is thoroughly ground and standards of lower boron content are prepared by dilution of the 10-p.p.m. standard with low-boron Nb_2O_5 . Alternately other standards may also be prepared by the addition of suitable boron standard solutions.

When the working curves are plotted, a correction is made for the residual boron content using the method of straight line approximation.

SPECTROGRAPHIC CONDITIONS

Spectrograph	Baird 3-meter
Setting	First order (2200 - 3700 A.)
Slit	25 micron
Lens	25-cm. lens focused on the grating
Grating	30-mm. exposure
Sector	Seven step 1:2 ratio
Excitation	10-1/2 amperes direct-current during smooth part of burn

Analytical Gap	4 mm
Upper Electrode	1/8-inch high-purity graphite with tip sharpened to a 90-degree included angle
Lower Electrode	National L4024 and L4042 pedestal. The electrode is loaded as described under Sample Preparation. The sample is the positive in the electrode circuit.
Exposure	Nominal exposure is 5 seconds preburn, 45 seconds exposure. This is performed manually for the start of the smooth or distillation burn occurs from 5 to 20 seconds after the start of the arc. Thirty seconds of smooth burn is desired and total exposure time may be increased for the occasional slow start
Emulsion	Spectrum Analysis #1
Development	3 minutes in D-19 at 70°C \pm 1°
Calibration	"Two iron line" method
Lines Used	B 2497.7. Background taken on high wave length side. Reading normally taken on the third step of the sectorized spectrum. As 2492.9. No background correction. Readings taken on the fourth step

REMARKS

The carrier distillation technique using gallium oxide does not work as well on Nb₂O₅ as it does with Ta₂O₅ and U₃O₈. The use of arsenic as an internal standard is helpful and works well most of the time. Occasionally, for reasons unknown, the arsenic will not show in the spectrum or will be very weak. In such cases it is necessary to calculate the results using an assumed value for the density of the arsenic line based on the average density of the line in the standards and other samples for that particular plate.

DETERMINATION OF CALCIUM AND MAGNESIUM IN NIOBIUM METAL OR OXIDE
(EMISSION SPECTROGRAPHIC METHOD)

SCOPE

This procedure is designed for the determination of from 0.003 to 0.1% MgO or CaO in Nb₂O₅.

PRINCIPLE OF METHOD

The oxide sample is mixed with graphite and analyzed using a high-voltage AC spark and a cap mix technique.

APPARATUS

Any commercial spectrograph with a dispersion of 6A/mm. and a direct-current excitation source is believed suitable for the determination. This procedure refers to the equipment listed below.

Spectrographic Apparatus

3-meter grating spectrograph	Baird Model AD-1
Source unit	Baird Model AK-3
Densitometer	Baird Model CD
Boron carbide mortar	
Pelleting press with 1/8-inch die	

PROCEDURE

A. PREPARATION OF THE SAMPLE

Place the finely-divided metal in a platinum or silica flat dish, and heat in a muffle furnace for one hour at 700 to 800°C. Select a portion of the converted oxide and grind in a large boron carbide mortar to obtain a representative sample. Samples of Nb₂O₅ of chemical origin should also be ground to ensure a representative sample.

Grind equal weights (70 mg.) of representative oxide and SP-1 graphite pelleting powder in a small boron carbide mortar. High-purity 1/8-inch spectroscopic graphite rod is notched with a sharp knife and broken into 3/16-inch lengths.* A scoopful of the oxide-graphite mix (about 18 milligrams) is pelleted on the rough fractured end of the graphite rod. The capped electrode is inserted in the end of a length of 1/4-inch diameter graphite rod containing a slightly tapered 1/8-inch diameter hole.

A 1/2-inch length of high-purity 1/8-inch diameter rod with a flat end is inserted in a piece of 1/4-inch rod and used as the counter electrode.

*Actually 3/8-inch cut lengths are broken in half.

B. PREPARATION OF STANDARDS

Suitable oxides of low calcium and magnesium content are dry-ground with pure CaO and MgO. Alternately standards may also be prepared by salting with appropriate calcium and magnesium standard solutions. A boron carbide mortar is used for the dry-grinding operation.

SPECTROGRAPHIC CONDITIONS

Spectrograph	Baird 3-meter												
Setting	First order 2600 to 4100 Å												
Slit	25-micron												
Lens	25-cm. focused on grating												
Sector	3 step 1:2 ratio												
Grating	10-mm. exposure												
Excitation	AC spark, 40-kilovolt setting, 0.00125 µF capacitance, 6 mH added inductance, 360 mH in parallel; 4 RF amperes, 3-ampere primary current. 10 to 12 breaks per half cycle.												
Upper electrode	1/8-inch diameter, high-purity graphite with flat end												
Lower electrode	Cap mix electrode												
Exposure	5-second preburn, 10-second exposure												
Development	3 minutes in D-19 at 70°F. ± 1°												
Calibration	"Two Iron Line" method for 2500 to 3200 Å region. Step sector method for 3900 to 4000 Å region.												
Line pairs used	For Nb ₂ O ₅ : <table><tr><td><u>Mg 2795</u></td><td>Steps 1 and 2</td></tr><tr><td>Nb 2816.67</td><td>Step 2</td></tr><tr><td><u>Ca 3933</u></td><td>Steps 1 and 2</td></tr><tr><td>Nb 3952.3</td><td>Step 2</td></tr><tr><td><u>Ca 3968</u></td><td>Steps 1 and 2</td></tr><tr><td>Nb 3952.3</td><td>Step 2</td></tr></table>	<u>Mg 2795</u>	Steps 1 and 2	Nb 2816.67	Step 2	<u>Ca 3933</u>	Steps 1 and 2	Nb 3952.3	Step 2	<u>Ca 3968</u>	Steps 1 and 2	Nb 3952.3	Step 2
<u>Mg 2795</u>	Steps 1 and 2												
Nb 2816.67	Step 2												
<u>Ca 3933</u>	Steps 1 and 2												
Nb 3952.3	Step 2												
<u>Ca 3968</u>	Steps 1 and 2												
Nb 3952.3	Step 2												

DETERMINATION OF TRACE ELEMENTS IN NIOBIUM METAL OR OXIDE
(ALUMINUM, LITHIUM, SILICON, TIN, TITANIUM, AND ZIRCONIUM)
(DIRECT EMISSION SPECTROGRAPHIC METHOD)

SCOPE

This procedure is designed for the direct determination of the elements listed below in niobium metal or oxide. Additional elements may be determined by the same procedure with the exception of strong carbide formers such as tungsten and molybdenum. Chemical concentration techniques such as ion exchange must be used in conjunction with this method for the determination of lower concentrations of tin, titanium, and zirconium.

Elements Determined

<u>Element</u>	<u>Range in Per Cent</u>
Silicon	0.0002* - 0.1
Aluminum**	0.003 - 0.1
Tin	0.003 - 0.1
Titanium	0.002 - 0.1
Zirconium	0.007 - 0.1
Lithium	0.0003 - 0.003

*Modification described in procedure for silicon below 0.005%.

**Refer to method for low concentrations of aluminum (3 to 100 p.p.m.) in niobium metal and oxide.

PRINCIPLE OF METHOD

Niobium metal is converted to oxide in a muffle furnace and the graphite-oxide mixture excited in a direct-current arc.

APPARATUS

Any commercial spectrograph with a dispersion of 6 A./mm. and a direct-current excitation source is believed suitable for this determination. This write-up refers to the equipment listed below.

Spectrographic Apparatus

3-meter grating spectrograph	Baird Model AD-1
Source unit	Baird Model AK-3
Densitometer	Baird Model CB
Boron carbide mechanical mortar	
Boron carbide hand mortar	

SPECIAL MATERIALS

Graphite Containing 1% GeO_2 and 0.25% PdCl_2 - Prepare by dry-grinding in a mechanical mortar a mixture of 900 mg. of high-purity SP-1 briquetting graphite and 100 mg. of $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ (Fisher Scientific). In the same manner, prepare a

10% GeO_2 in graphite mixture. Dilute these and blend succeeding mixtures with graphite to make a concentration of 1% GeO_2 and 0.25% PdCl_2 . At no time is a greater dilution than 1:9 employed.

PROCEDURE

A. PREPARATION OF SAMPLE

Place finely divided metal in a platinum or silica dish and heat in a muffle furnace for one hour at 700°C . With coarse material, the use of oxygen during the furnace treatment is often helpful. The converted oxide should be ground in a boron carbide mortar or other device to ensure a representative sample. Because of the abrasive qualities of niobium oxide, careful selection of the grinding device and its operation is required in order to minimize contamination. Oxide samples of chemical origin should also be ground to ensure a representative sample.

Select a portion of the ground oxide and mix with one part by weight of graphite containing 1% GeO_2 and 0.25% PdCl_2 in a small hand boron carbide mortar. The electrodes are loaded with the graphite mix and the upper surface scraped flush with the blade edge of the spatula. The sample is excited under the conditions described.

For the determination of silicon in niobium of the highest purity (<50 p.p.m. of silicon), the graphite containing 1% GeO_2 and 0.25% PdCl_2 is omitted and plain graphite only used. This is because of the difficulty of preparing the internal standard mixture absolutely free of silicon. Also, for the lithium determination, only plain graphite is used.

Samples for the lithium determination are prepared by a different method. One gram of niobium metal is dissolved in hydrofluoric and nitric acids. When all the metal is dissolved, sulfuric acid is added and the solution brought to fumes. As much of the sulfuric acid as possible is evaporated on the hot plate before placing in a muffle. The temperature is gradually raised to 700 to 800°C . and baked for one-half hour. Afterward it is cooled, ground, and mixed with graphite as previously described.

B. PREPARATION OF STANDARDS

Standards are prepared by dry-grinding oxides of the elements with suitably pure niobium oxide. Often two or more sets of standards containing the same, but different combinations of other elements are available for cross checking. Alternately, standards for selected elements may be prepared by using chemical precipitation techniques. These may consist of oxide made from ammonia or cupferron precipitates of salted solutions.

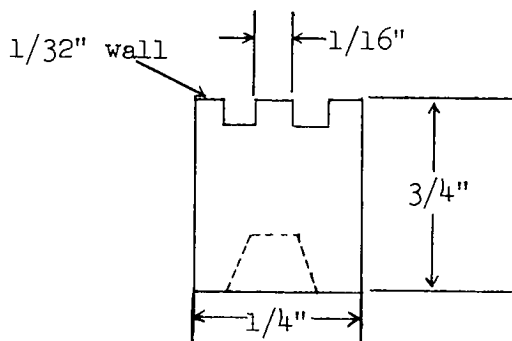
Except for lithium, there was no difference detected between chemically-prepared oxides and those prepared by air oxidation of the metal.

Standards for lithium were prepared by adding appropriate amounts of lithium standard solution (prepared by dissolving lithium carbonate in dilute nitric acid) to a HF-HNO_3 solution of lithium-free niobium metal as described under Preparation of Samples.

SPECTROGRAPHIC CONDITIONS

(All elements except lithium)

Spectrograph	Baird 3-meter
Setting	First order (2200 to 3700 Å)
Slit	25 micron
Lens	25-cm. focused on grating
Grating	3-mm. exposed, increase to 5 mm. for trace silicon determination
Sector	Two-step sector adjusted for full and 1/4 exposure
Excitation	10-1/2 amperes, direct-current, sample positive
Analytical gap	4 mm.
Upper electrode	1/8-inch high-purity graphite with the tip sharpened to a 90-degree included angle
Lower electrode	



Exposure	Thirty seconds, no preburn																								
Development	3 minutes in D-19 at 70°F ± 1°																								
Emulsion	Spectrum Analysis #1																								
Calibration	"Two Iron Line" method																								
Line pairs used	<u>Elements in Nb₂O₅</u> <table> <tr> <td>Silicon.</td> <td><u>Si 2528</u></td> <td>Full sector, BG* high side</td> </tr> <tr> <td></td> <td><u>Ge 2533.3</u></td> <td>1/4 sector</td> </tr> <tr> <td></td> <td><u>Si 2528</u></td> <td>1/4 sector</td> </tr> <tr> <td></td> <td><u>Ge 2533.3</u></td> <td>1/4 sector</td> </tr> <tr> <td></td> <td><u>Si 2516**</u></td> <td>Full sector, BG high side</td> </tr> <tr> <td></td> <td><u>D = 50</u></td> <td></td> </tr> <tr> <td></td> <td><u>Si 2528**</u></td> <td>Full sector, BG high side</td> </tr> <tr> <td></td> <td><u>D = 50</u></td> <td></td> </tr> </table>	Silicon.	<u>Si 2528</u>	Full sector, BG* high side		<u>Ge 2533.3</u>	1/4 sector		<u>Si 2528</u>	1/4 sector		<u>Ge 2533.3</u>	1/4 sector		<u>Si 2516**</u>	Full sector, BG high side		<u>D = 50</u>			<u>Si 2528**</u>	Full sector, BG high side		<u>D = 50</u>	
Silicon.	<u>Si 2528</u>	Full sector, BG* high side																							
	<u>Ge 2533.3</u>	1/4 sector																							
	<u>Si 2528</u>	1/4 sector																							
	<u>Ge 2533.3</u>	1/4 sector																							
	<u>Si 2516**</u>	Full sector, BG high side																							
	<u>D = 50</u>																								
	<u>Si 2528**</u>	Full sector, BG high side																							
	<u>D = 50</u>																								

*This means background correction taken on higher wave length side of line.
 **Used for very low silicon determination.

Line pairs used
(cont.)

Elements in Nb₂O₅

Aluminum	<u>Al 3082</u> <u>Pd 3258</u>	Full sector, BG high side
Tin:	<u>Sn 3175</u> <u>Ge 2533</u>	Full sector, BG low side 1/4 sector
	<u>Sn 2429</u> <u>Ge 2533</u>	Full sector, BG high side 1/4 sector
Titanium	<u>Ti 3078</u> <u>Pd 3258</u>	Full sector, BG high side 1/4 sector
	<u>Ti 3078</u> <u>Pd 3258</u>	1/4 sector 1/4 sector
	<u>Ti 3106.234</u> <u>Pd 3258</u>	1/4 sector 1/4 sector
Zirconium	<u>Zr 3391.8</u> <u>Pd 3258</u>	Full sector, BG low side 1/4 sector

SPECTROGRAPHIC CONDITIONS FOR LITHIUM

Spectrograph	Baird 3-meter
Setting	First order (5300 to 6800 Å)
Slit	50 micron
Lens	25-cm. focused on grating
Sector	3-step, 1:2 ratio
Grating	30-mm. exposed
Excitation	6 amperes, direct-current, sample positive
Analytical gap	4 mm.
Upper and lower electrode:	Same as regular method
Exposure	Twenty seconds, no preburn
Emulsion	Eastman Kodak, IN
Development	3 minutes in D-19 at 70°F. ± 1°
Calibration	Step sector at 6000 Å.
Line pairs used	<u>Li 6707.8</u> Background

The lithium line is densitometered in the second step of the three-step spectra. The background is read on the same step on the higher wave length side of the line. The ratio of the net intensity of the lithium line corrected for background to the intensity of the background is plotted versus concentration.

DETERMINATION OF ZIRCONIUM, TITANIUM, VANADIUM, AND TIN IN NIOBIUM
(ION EXCHANGE SEPARATION-EMISSION SPECTROGRAPHIC METHOD)

SCOPE

This procedure is designed for the determination of zirconium, titanium, vanadium, and tin in the range of 0.5 to 20 p.p.m.

PRINCIPLE OF METHOD

The zirconium, titanium, vanadium, and tin are separated from niobium on an ion exchange column containing Dowex 1 resin. The oxides are precipitated with cupferron using high-purity tantalum as a carrier. They are then determined emission spectrographically by excitation in a direct-current arc. Tungsten and molybdenum cannot be determined by this method.

CONCENTRATION RANGE

The following elements collected in a tantalum oxide matrix have the sensitivity as listed. However, since a 5.0-gram sample of niobium is taken and the elements concentrated into 0.1 gram of Ta_2O_5 for the spectrographic determination, the sensitivity is actually 1/50 of that tabulated.

<u>Element</u>	<u>Range (%) in Ta_2O_5 Matrix</u>
Tin	0.002 - 0.1
Titanium	0.002 - 1.0
Vanadium	0.002 - 0.1
Zirconium	0.002 - 0.5

SPECIAL APPARATUS

1 The columns are constructed of polystyrene and are approximately 18 inches long and one inch I.D. The bottom of the tube is closed by a waxed No. 5 rubber stopper with a 3/16-inch hole. A 6-inch length of polystyrene tubing with a 3/16-inch O.D. is inserted in the hole. A 3-inch length of Tygon tubing is attached and the flow controlled by a hose cock on the Tygon tubing.

2. The resin is Dowex 1, 200 to 400 mesh, 8 to 10% divinylbenzene cross-linkage. Prepare a suspension of the resin in dilute HCl (1:19). Allow the coarser fraction to settle 10 to 15 minutes and remove the fines by decantation. Repeat the process about 7 to 8 times until most of the fine material is removed from the suspension.

3. The bottom of the ion exchange is covered with a 1/4- to 3/8-inch layer of acid-resistant vinyl chloride plastic wool (Dynel). Add the suspension of resin in one addition. Sufficient resin should be present to form a settled column 12 inches high. The loaded column should be run through several cycles of alternate elution with HCl (3:1) and HCl (1:9) to remove the fines. The column is then washed with HCl (1:3) and is ready for use. At no time should the column be allowed to run dry. The flow rate should be about 100 to 125 ml. per hour

4. Polyethylene Water - 400-, 600-, and 1000-ml. beakers and bottles for preparing and dispensing acid mixtures.

REAGENTS

Hydrochloric-hydrofluoric Acid Solution - Add 250 ml. of HCl to 300 ml. of water, add 200 ml. of HF, and dilute to one liter with water.

Standard Ammonium Chloride Solution - Dissolve 240 g. of NH_4Cl in 800 ml. of water and dilute to one liter with water.

Titanium, Tin, Vanadium, and Zirconium Eluant - To 300 ml. of the ammonium chloride solution, add 200 ml. of HF and 125 ml. of HCl, and dilute to one liter with water.

Niobium and Tantalum Eluant - To 600 ml. of the ammonium chloride solution, add 40 ml. of HF. Adjust the pH to 5.5 to 6.5 with NH_4OH . (Approximately 80 to 85 ml. will be required). Dilute to one liter with water (Note 1).

SPECTROGRAPHIC APPARATUS

Any commercial spectrograph with a dispersion of 6 A./mm. and a direct-current excitation source is believed suitable for this determination. This procedure refers to the equipment listed below.

Spectrographic Apparatus

3-meter grating spectrograph	Baird Model AD-1
Source unit	Baird Model AK-3
Densitometer	Baird Model CB
Boron carbide hand mortar	

SPECIAL MATERIALS FOR SPECTROGRAPHIC ANALYSIS

Graphite Containing 1% GeO_2 and 0.25% PdCl_2 - Prepare by dry-grinding in a mechanical mortar a mixture of 900 mg. of high-purity SP-1 briquetting graphite and 100 mg. of $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ (Fisher Scientific). In the same manner, prepare a 10% GeO_2 in graphite mixture. Dilute these and blend succeeding mixtures with graphite to make a concentration of 1% GeO_2 and 0.25% PdCl_2 . At no time is a greater dilution than 1:9 employed.

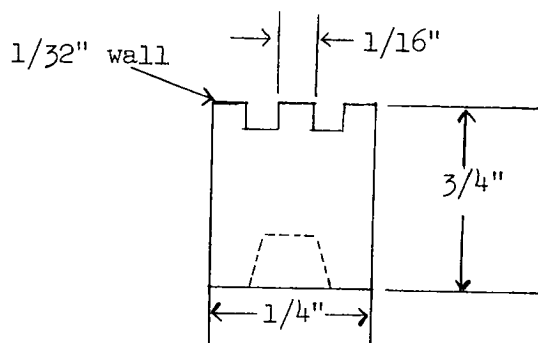
PREPARATION OF EMISSION SPECTROGRAPHIC STANDARDS

Standards are prepared by dry-grinding oxides of the elements with suitably pure tantalum oxide. Often two or more sets of standards containing the same but different combinations of other elements are available for cross checking. Where chemical concentration techniques are employed, additional standards are prepared using similar chemical procedures. For example, oxides may be prepared from cupferron precipitates of salted solutions or may be derived from salted solutions carried through the entire concentration operation.

It is desirable to prepare standards as per cent element in the oxide. Thus, if the residual elements in a 5-gram sample of niobium metal are collected in a Ta_2O_5 precipitate of 0.1 gram, the original concentration is $1/50$ of that in the precipitate, and results read from the working curves are multiplied by this fraction.

SPECTROGRAPHIC CONDITIONS

Spectrograph	Baird 3-meter
Setting	First order (2200 to 3700 Å)
Slit	25-micron
Lens	25-cm. focused on grating
Grating	3-mm. exposed
Sector	2 step sector adjusted for full and $1/4$ exposure
Excitation	10-1/2 amperes, direct-current sample positive
Analytical gap	4-mm.
Upper electrode	1/8-inch high-purity graphite with the tip sharpened to a 90-degree included angle
Lower electrode	



Exposure	Thirty seconds, no preburn																																				
Development	3 minutes in D-19 at 70°F. $\pm 1^\circ$																																				
Emulsion	Spectrum Analysis No. 1																																				
Calibration	"Two iron line" method																																				
Line pairs used	Elements in Ta ₂ O ₅																																				
	<table> <tbody> <tr> <td><u>Sn 3175</u></td> <td>Full sector B.G.* low side</td> </tr> <tr> <td><u>Ge 2533</u></td> <td>1/4 sector</td> </tr> <tr> <td><u>Sn 3009</u></td> <td>Full sector B.G. low side</td> </tr> <tr> <td><u>Ge 2533</u></td> <td>1/4 sector</td> </tr> <tr> <td><u>Tl 3239.0</u></td> <td>Full sector B.G. high side</td> </tr> <tr> <td><u>Pd 3258</u></td> <td>1/4 sector</td> </tr> <tr> <td><u>Tl 3078.6</u></td> <td>Full sector B.G. high side</td> </tr> <tr> <td><u>Pd 3258</u></td> <td>1/4 sector</td> </tr> <tr> <td><u>Tl 3202.5</u></td> <td>Full sector B.G. high side</td> </tr> <tr> <td><u>Pd 3258</u></td> <td>1/4 sector</td> </tr> <tr> <td><u>Tl 3202.5</u></td> <td>1/4 sector</td> </tr> <tr> <td><u>Pd 3258</u></td> <td>1/4 sector</td> </tr> <tr> <td><u>Zr 3391.9</u></td> <td>Full sector B.G. high side</td> </tr> <tr> <td><u>Pd 3258</u></td> <td>1/4 sector</td> </tr> <tr> <td><u>V 3183.9</u></td> <td>Full sector B.G. low side</td> </tr> <tr> <td><u>Pd 3258</u></td> <td>1/4 sector</td> </tr> <tr> <td><u>V 3183.4</u></td> <td>Full sector B.G. low side</td> </tr> <tr> <td><u>Pd 3258</u></td> <td>1/4 sector</td> </tr> </tbody> </table>	<u>Sn 3175</u>	Full sector B.G.* low side	<u>Ge 2533</u>	1/4 sector	<u>Sn 3009</u>	Full sector B.G. low side	<u>Ge 2533</u>	1/4 sector	<u>Tl 3239.0</u>	Full sector B.G. high side	<u>Pd 3258</u>	1/4 sector	<u>Tl 3078.6</u>	Full sector B.G. high side	<u>Pd 3258</u>	1/4 sector	<u>Tl 3202.5</u>	Full sector B.G. high side	<u>Pd 3258</u>	1/4 sector	<u>Tl 3202.5</u>	1/4 sector	<u>Pd 3258</u>	1/4 sector	<u>Zr 3391.9</u>	Full sector B.G. high side	<u>Pd 3258</u>	1/4 sector	<u>V 3183.9</u>	Full sector B.G. low side	<u>Pd 3258</u>	1/4 sector	<u>V 3183.4</u>	Full sector B.G. low side	<u>Pd 3258</u>	1/4 sector
<u>Sn 3175</u>	Full sector B.G.* low side																																				
<u>Ge 2533</u>	1/4 sector																																				
<u>Sn 3009</u>	Full sector B.G. low side																																				
<u>Ge 2533</u>	1/4 sector																																				
<u>Tl 3239.0</u>	Full sector B.G. high side																																				
<u>Pd 3258</u>	1/4 sector																																				
<u>Tl 3078.6</u>	Full sector B.G. high side																																				
<u>Pd 3258</u>	1/4 sector																																				
<u>Tl 3202.5</u>	Full sector B.G. high side																																				
<u>Pd 3258</u>	1/4 sector																																				
<u>Tl 3202.5</u>	1/4 sector																																				
<u>Pd 3258</u>	1/4 sector																																				
<u>Zr 3391.9</u>	Full sector B.G. high side																																				
<u>Pd 3258</u>	1/4 sector																																				
<u>V 3183.9</u>	Full sector B.G. low side																																				
<u>Pd 3258</u>	1/4 sector																																				
<u>V 3183.4</u>	Full sector B.G. low side																																				
<u>Pd 3258</u>	1/4 sector																																				

PROCEDURE

Transfer 5.00 g. of the sample to a 300-ml. platinum casserole. Add 25 to 50 ml. of hydrofluoric acid, cover with a platinum or Teflon cover, and add nitric acid dropwise until the sample is dissolved. Evaporate on a steam bath until almost dry. Add 10 ml. of hydrofluoric acid, 1 ml. of formic acid, and evaporate again until almost dry (Note 2). Add 100 ml. of the hydrofluoric-hydrochloric acid solution and warm gently to obtain a clear solution.

*This means that the background reading is taken on lower wave length side of the tin line.

Transfer 50 ml. of the hydrochloric-hydrofluoric acid solution to the column in small increments (5 to 10 ml.) and drain the acid to 1 cm. above the resin bed. Place a 600-ml. polyethylene beaker under the column.

Cool the sample and transfer to the column in small increments (5 to 10 ml.). Wash the platinum dish 4 to 5 times with 5-ml. portions of the hydrochloric-hydrofluoric solution, transferring the washings to the column. Wash down the sides of the column several times using approximately 50 ml. of the hydrochloric acid-hydrofluoric acid solution. Drain to 1 ml. above the resin bed and catch the eluate in the 600-ml. polyethylene beaker.

Keep the same beaker under the column and add 300 ml. of the titanium eluant at a flow rate of 100 to 125 ml. per hour. Allow the solution to drain to the top of the resin and wash the sides of the column five times with 5-ml. portions of the niobium eluant, allowing the solution to drain to the top of the column each time. Save for the determination of titanium. It contains the titanium, iron, vanadium, tin, zirconium, etc. The column is cleaned by the addition of 400 ml. of the niobium-tantalum eluant followed by 50 ml. of HCl (1.3) and is then ready for the next sample (note 3).

Transfer 40 g. of boric acid to a 1500-ml. beaker, add 700 ml. of water, and warm to dissolve the acid. Transfer 0.100 g. of high-purity tantalum metal to a 50-ml. platinum dish and add 3 ml. of hydrofluoric acid and nitric acid dropwise until the metal is all in solution. Evaporate to a low volume. Transfer the tantalum solution to the eluate reserved in the polyethylene beaker. Transfer the eluate to the boric acid solution. Cool to 5°C. and add, with stirring, 100 to 125 ml. of the cupferron solution for a complete precipitation. Add paper pulp, stir the solution and allow the precipitate to settle for 10 minutes. Filter on a Büchner funnel and wash with about 400 ml. of the cupferron wash solution. Transfer to a platinum dish and ignite at a low temperature and then at about 500 to 600°C. until all the carbon is burned off. Ignite finally at 900°C. for one hour. Cool, place in a desiccator and reserve for the determination of the elements by emission spectroscopy.

The ignited oxide from the ion-exchange procedure is weighed to determine the concentration factor (original sample weight/weight of oxide). The oxide is then ground in a hand boron carbide mortar to ensure a representative sample. A portion of the ground oxide is then mixed with an equal weight of graphite containing 1% GeO_2 and 0.25% PdCl_2 in a boron carbide hand mortar. The electrodes are loaded with the graphite mix and the upper surface scraped flush with the blade edge of the spatula. The electrode is placed in the spectrograph and the sample excited under the conditions described. Calculate the concentration of elements present in the Ta_2O_5 oxide concentrate by reference to the appropriate calibration graph. Determine the concentration of elements in the original sample by dividing by the concentration factor.

NOTES

1. This solution should be prepared with care. If the solution is too acid, tantalum will not be completely eluted in the volume specified. If the eluant is too alkaline, tantalum will precipitate in the column spoiling the determination being run and the one to follow.

2. The nitric acid must be removed, otherwise, the niobium will not be completely retained on the column. Some of the niobium will end up with the oxide to be analyzed and will interfere with the spectrographic determination.

3. Periodically the columns must be repacked because of a change in the physical form of the column. After several weeks of use, channeling occurs and niobium begins to pass through into the eluate. When this occurs, the resin should be removed from the column, reslurried, and returned to the column.

APPENDIX III - MISCELLANEOUS ANALYTICAL METHODS

DETERMINATION OF LOW CARBON IN NIOBIUM METAL

SCOPE

This procedure is suitable for the determination of carbon in low amounts (p.p.m.) in niobium metal.

PRINCIPLE OF METHOD

The method involves combustion of the sample in the presence of an accelerator in a stream of purified oxygen. The oxygen containing the carbon dioxide is passed through a conductometric apparatus for measurement of the carbon dioxide.

APPARATUS

- a. Burrell two-tube Globar furnace equipped with two 1-inch (I.D.) x 27-inch McDaniel tubes and a platinum, platinum-rhodium thermocouple. One tube is operated with open ends for free access of air for prefiring boats. The inlet and outlet glass tubes for the oxygen in the sample tube are flared to serve as radiation shields for the rubber stoppers.
- b. Leco Conductometric Unit Model 515
- c. Oxygen purification system consisting of copper oxide furnace operating at 350°C., Ascarite - magnesium perchlorate tower, surge tank and pressure control valve. The surge tank is incorporated to ensure a flow of oxygen through the tube even at the height of the burn.
- d. Leco No. 5 boats
- e. MnO₂ tower between the furnace and conductometric apparatus (Leco or Fisher special MnO₂)

REAGENTS

- a. 30-mesh tin
- b. Barium hydroxide solution according to Leco instructions

PROCEDURE

- a. Raise the temperature of the furnace to 1425 to 1450°C. (as measured in the external thermowell) and the conductometric apparatus and solution to temperature.
- b. Prefire a boat in the auxiliary tube for at least five minutes. Remove the boat and cool (while covered) on a clean metal plate to < 200°C.
- c. Transfer 2.0 g. of the tin shot to the boat and insert in the hot zone of the furnace. (The tin can be measured volumetrically with sufficient accuracy.)

- d. Start the oxygen flow through the furnace and adjust to 325 to 330 ml. per minute and null the conductometric apparatus. This must be done within 30 seconds after insertion of the sample.
- e. After 10 minutes, balance the bridge, record the resistance, drain, and replace with fresh $\text{Ba}(\text{OH})_2$ solution.
- f. Repeat steps b and c until a consistent blank is obtained.
- g. To prepare a calibration curve, transfer 0.500 g. of a suitable standard (0.02 to 0.07% carbon) to a prefired boat, cover with 2.0 g. of tin, and repeat steps c to e. Repeat until consistent values are obtained on the standard. Carry out this procedure with other standards in this range or by burning fractional weights of a single standard.
- h. Plot the resistance change of the blank and standards versus per cent carbon on linear graph paper.
- i. Transfer 0.500 g. of the sample (1.00 g. for $< 0.015\%$ carbon) to a prefired boat and repeat steps c to e.
- j. Determine the per cent carbon from the calibration curve.

There may be a small but consistent curve shift during a day's operation. A standard and blank should be checked at the beginning, middle, and end of an 8-hour day.

The balancing of the bridge after insertion of the sample is permissible since the CO_2 from the combustion does not reach the conductance bridge until about 90 seconds have elapsed.

The use of ceramic pedestals ($5/8 \times 4-1/4$ inch) under the boats will protect the tube. These must also be prefired but can be used repeatedly. (Available from the McDanel Company).

DETERMINATION OF NITROGEN IN NIOBIUM METAL
(DISTILLATION - TITRIMETRIC METHOD)

SCOPE

This method is applicable to niobium metal containing more than 0.005% nitrogen.

PRINCIPLE OF METHOD

The sample is dissolved in HF plus H_2O_2 , thus converting the nitrides to the ammonium salt. The ammonium is steam distilled out of the alkaline solution into boric solution and titrated with standard acid.

SPECIAL APPARATUS

Micro-Kjeldahl apparatus as described in Analytical Chemistry 23, 523 (1951) except the digestion flask has a volume of 150 ml.

SPECIAL SOLUTIONS

NaOH Solution - Dissolve 400 g. of NaOH in one liter of water.

Boric Acid Solution - Dissolve 20 g. of H_3BO_3 in one liter of hot distilled water and cool.

Mixed Indicator - Dissolve 0.10 g. of bromocresol green in 10 ml. of methanol and 0.02 g. of methyl red in another 10-ml. portion of methanol. Dilute the two solutions to 50 ml. each with methanol and combine.

0.00714N H_2SO_4 - This is standardized against 0.01N NaOH which has been freshly standardized against N.B.S. 84 potassium acid phthalate.

PROCEDURE

Solution of Sample

Transfer 1.00 g. of the sample (mullings or drillings) to a 100-ml. platinum dish, add 5 ml. of HF and 15 drops of H_2O_2 (30%). Heat carefully, supplying just enough heat to keep the reaction going. When dissolution is complete, add 150 mg. of H_3BO_3 and digest until the solution is clear.

Run a blank on all the reagents. Since the water contains small amounts of nitrogen, the amount of water used for dilution and washing should be measured so that the blank will be comparable to the sample.

Cool and transfer the solution of the sample to the digestion flask of the microdistillation apparatus. The outlet tube of the condenser should dip into 5 ml. of the boric acid solution containing 5 drops of the mixed indicator in a 125-ml. Erlenmeyer flask. Add 30 ml. of the NaOH solution to the digestion flask

and admit steam. The distillation is complete three minutes after the first condensate appears. Drop the Erlenmeyer flask until the outlet tube is approximately one centimeter above the surface of the solution. Continue the distillation for one minute more.

Titrate the boric acid solution with the standardized H_2SO_4 solution using a 5-ml. buret.

$$\% \text{ Nitrogen} = (A - B) (0.01)$$

where A = ml. of 0.00714N H_2SO_4 used for sample

B = ml. of 0.00714N H_2SO_4 used for blank

DETERMINATION OF NITROGEN IN NIOBIUM METAL
(DISTILLATION - SPECTROPHOTOMETRIC METHOD)

SCOPE

This method is designed for the determination of from 0.0001 (1 p.p.m.) to 0.02% nitrogen in niobium.

PRINCIPLE OF METHOD

The sample of niobium is dissolved in HF and H₂O₂. The solution is made basic with sodium hydroxide and the ammonia steam-distilled into a buffered solution. Chloramine-T solution and pyridine-pyrazolone reagent are added to the buffered solution and the colored complex containing the ammonia is extracted with carbon tetrachloride and measured colorimetrically at 450 m μ .

CONCENTRATION RANGE

The range of the colored system using a 1-cm. cell is from 0.01 to 0.1 mg. of nitrogen in 50 ml. of solution. The system follows Beer's Law up to an absorbance of 1.0, but deviates slightly at higher absorbance values.

The range of the colored system using a 5-cm. cell is from 0.002 to 0.02 mg. of nitrogen in 50 ml. of solution.

SPECIAL SOLUTIONS

Ammonia-Free Water - Slowly pass distilled water through Dowex 50 ion exchange resin.

Buffer - Transfer 13.6 g. of sodium acetate and 61.5 ml. of glacial acetic acid in a one-liter volumetric flask and dilute to the mark with ammonia-free water. The pH of the buffer should be between 3.2 and 3.8.

Chloramine-T - Dissolve 0.6 g. in 22 ml. of ammonia-free water. Prepare fresh before use. Store the solid reagent in a dark place. The solid reagent sometimes deteriorates upon standing and after a year it may lose its effectiveness as a reagent.

Pyrazolone - Dissolve 0.63 g. of 3-methyl-1-phenyl-5-pyrazolone (Eastman Organic Chemicals 1397), recrystallized from alcohol, in 250 ml. of ammonia-free water by heating to 75°C. and allowing to cool.

3,3'-Dimethyl-1,1'-Diphenyl-(4,4'-bi-2-pyrazoline)-5,5'-dione /bispyrazolone/
- Eastman Organic Chemicals 6969 - To prepare this solution for the composite pyridine-pyrazolone reagent, dissolve 0.050 gram of bispyrazolone in 50 ml. of pyridine by allowing to stand 45 minutes. This solution is not stable and should be made just prior to use.

Pyridine-Pyrazolone Reagent - Mix 250 ml. of the pyrazolone solution with 50 ml. of the freshly prepared bispyrazolone-pyridine solution. This reagent should be prepared not more than 15 minutes prior to use.

Sodium Hydroxide Solution - Add 500 ml. of ammonia-free water to 500 g. of NaOH pellets. Boil with 2 grams of Devarda's alloy for 10 minutes. The solution does not need to be filtered from the alloy.

Standard Solution of Ammonium Sulfate - Dissolve 0.2358 g. of $(\text{NH}_4)_2\text{SO}_4$ in approximately 500 ml. of ammonia-free water and dilute to one liter. This stock solution contains 0.05 mg. of nitrogen per ml. Transfer 25 ml. of the stock solution to a 250-ml. volumetric flask and dilute to the mark with ammonia-free water to make a solution containing 0.005 mg. of nitrogen per ml.

SPECIAL APPARATUS

The apparatus used for the distillation of the ammonia corresponded to the Kjeldahl semi-microapparatus, Fisher Catalog No. 59, Part No. 21-101, with the modification of replacing the vacuum jacket with a 300-ml. Kjeldahl flask adapted with a 24/42 ground glass connection. Of special importance is the use of the silver condenser, Fisher Catalog No. 94, Part No. 21-110.

PREPARATION OF CALIBRATION GRAPH

Transfer 2, 5, 10, 15, and 20 ml. portions of the dilute standard ammonium sulfate solution (0.005 g. of nitrogen per ml.) to 125-ml. Erlenmeyer flask. Add 10 ml. of the buffer solution to each flask and to a flask containing no ammonium sulfate to be carried through the procedure as a blank on the reagents. Add water to each flask to bring the total volume of the solution to about 50 ml. Add 1.0 ml. of the Chloramine-T solution from a buret and mix. After 90 seconds, add 30 ml. of pyridine-pyrazolone reagent and mix. A pink color indicates the presence of ammonia. Allow to stand for at least two minutes (but not more than 15 minutes). Transfer the solution to a 250-ml. separatory funnel. Extract twice with 15-ml. portions of carbon tetrachloride. Collect the CCl_4 layers in a 50-ml. flask and dilute to the mark with ethanol and mix. Measure the absorbance at 450 m μ in a spectrophotometer with a 1-cm. cell using the blank as null. Plot absorbance versus concentration.

If very low nitrogen concentrations (< 0.01 mg.) are to be measured, 5-cm. cells should be used instead of 1-cm. cells.

PROCEDURE

Transfer 1.00 g. of the 100-mesh sample containing from 1 to 100 micrograms of nitrogen to a 100-ml. platinum dish, add 5 ml. of HF and 15 drops of H_2O_2 (30%). Heat carefully, supplying just enough heat to keep the reaction going. When dissolution is complete, add 150 mg. of H_3BO_3 and digest until the solution is clear.

Determine a blank on all the reagents.

Cool and transfer the solution of the sample to the digestion flask of the microdistillation apparatus.

DISTILLATION OF AMMONIA AND DEVELOPMENT OF COLOR

Wash down the sides of the flask with 100 ml. of water and cool. Place 10 ml. of the buffer solution in the distillate trap. Attach the flask to the apparatus by means of a ball joint tension clamp. Carefully add 40 ml. of 50% sodium hydroxide and steam distill, collecting 40 ml. of distillate. Develop the color as described in the Preparation of Calibration Graph.

REFERENCES

1. Kruse, J. M., and Mellon, M. G., Anal. Chem. 25, 1188 (1953)
2. Lear, J. B., and Mellon, M. G., Anal. Chem. 29, 293 (1957)

DETERMINATION OF OXYGEN AND HYDROGEN IN NIOBIUM METAL
(MICRO VACUUM-FUSION METHOD USING PLATINUM FLUX TECHNIQUE)

SCOPE

This method is suitable for the determination of oxygen and hydrogen in niobium metal and related alloys in the 0 to 500 p.p.m. range. (See Note 1)

PRINCIPLE OF METHOD

This method is based on fusion of the sample with platinum in a graphite crucible in a high-frequency vacuum furnace. Thus, the oxide is reduced by the carbon, and the oxygen is evolved as CO. Under the conditions of the high temperature and the high vacuum, nitrides are decomposed and N₂ liberated. Likewise, hydrogen is extracted from the sample as H₂. This mixture of CO, H₂, and N₂ is collected in a constant, calibrated volume, and the percentages of the three determined by differential pressure measurements.

APPARATUS

Basically, the apparatus consists of a high-frequency furnace built around a quartz tube, three glass mercury diffusion pumps and accessory glassware for collecting and analyzing the gas together with suitable backing-up pumps for out-gassing the system. A view of the apparatus is shown in Figure 1. Similar apparatus and methods have been described in the literature (1, 2, 3, 4).

Power Supply - A 15-kw. Tocco motor generator is used as a source of high-frequency power.

Furnace - The graphite crucible is heated by nine turns of double 1/4-inch water-cooled copper tubing wound as closely as possible around the quartz tube but not touching it. This serves as the primary and carries the high-frequency current from the motor generator. The vertical silica tube extends through the copper coil and rests on a pedestal. The standard tube is 18 by 2-7/8 inches O.D. by 2-3/8 inches I.D., made with a round bottom with an integral closure. The top is closed with a brass head attached with deKhotinsky cement. Samples are introduced into the furnace through a turret cap which fits on this head and is sealed with a 1/8- x 3-inch "O" ring and tightened with thumb screws. The glass tubes are approximately 8 inches long and are cemented in the turret nipples with deKhotinsky cement. Samples are placed in the glass tubes and dropped into the furnace by means of a brass-tipped ferritic stainless steel pusher manipulated with an Alnico magnet.

Crucible - The crucible is machined of high-purity graphite (Note 2). The samples are guided into the crucible with a graphite funnel. The arrangement of the crucible, thimble, etc., in the furnace is as follows

A 2- x 6-1/2-inch clear quartz thimble with two 1/8-inch holes near the top and opposite each other for lowering it into place is prepared.

200 M x D graphite is placed in the quartz thimble to a depth of approximately 4-1/2 to 5 inches. The graphite crucible is carefully centered in this graphite powder to a depth of about 3 inches. Coarse graphite chips (+20M) are

then placed on top of the powder to the top of the graphite crucible. These chips serve to prevent the powder from blowing out of the thimble during the initial degassing operation.

This assembly is then lowered into the quartz tube where it rests on a 1- to 2-inch layer of quartz chips. The graphite funnel is next placed in position in the mouth of the crucible. A copper funnel rests in the top of the brass head and serves to guide samples into the graphite funnel. (See Figure 2)

Vacuum Pumping System - One two-stage and one three-stage glass mercury diffusion pump with a high capacity and high backing-up pressure, respectively, are connected to the brass head with 1-1/2-inch Pyrex tubing and ball and socket joint. The pumps are heated electrically. The output of the three-stage pump feeds into an automatic Toepler pump which compresses the gases into one of several calibrated volumes. There are by-passes in this system for McLeod, Todd and Piranni gauges, and for a third diffusion pump and mechanical pump for initial pumping out of the system.

PROCEDURE

Sample preparation - see Note 3

Place samples and platinum in the side arms of the furnace head. Close the furnace and evacuate. Heat the graphite crucible to 2300 to 2500°C. for approximately 4 to 5 hours. Vent the gas collected during this period to the atmosphere. Turn off the power, allow the crucible to cool to approximately 1500°C., shut off the system from the atmosphere, and determine the blank by dropping a piece of platinum equal in weight to platinum wrapped with sample. When a satisfactory blank is obtained, drop the samples with platinum successively and collect the gases evolved in the calibrated volume and analyze. A 10- to 15-minute fusion time is normal for most samples. The crucible is cooled to 1500°C. between each sample introduction and then the temperature is raised to 2000°C. to ensure complete reduction.

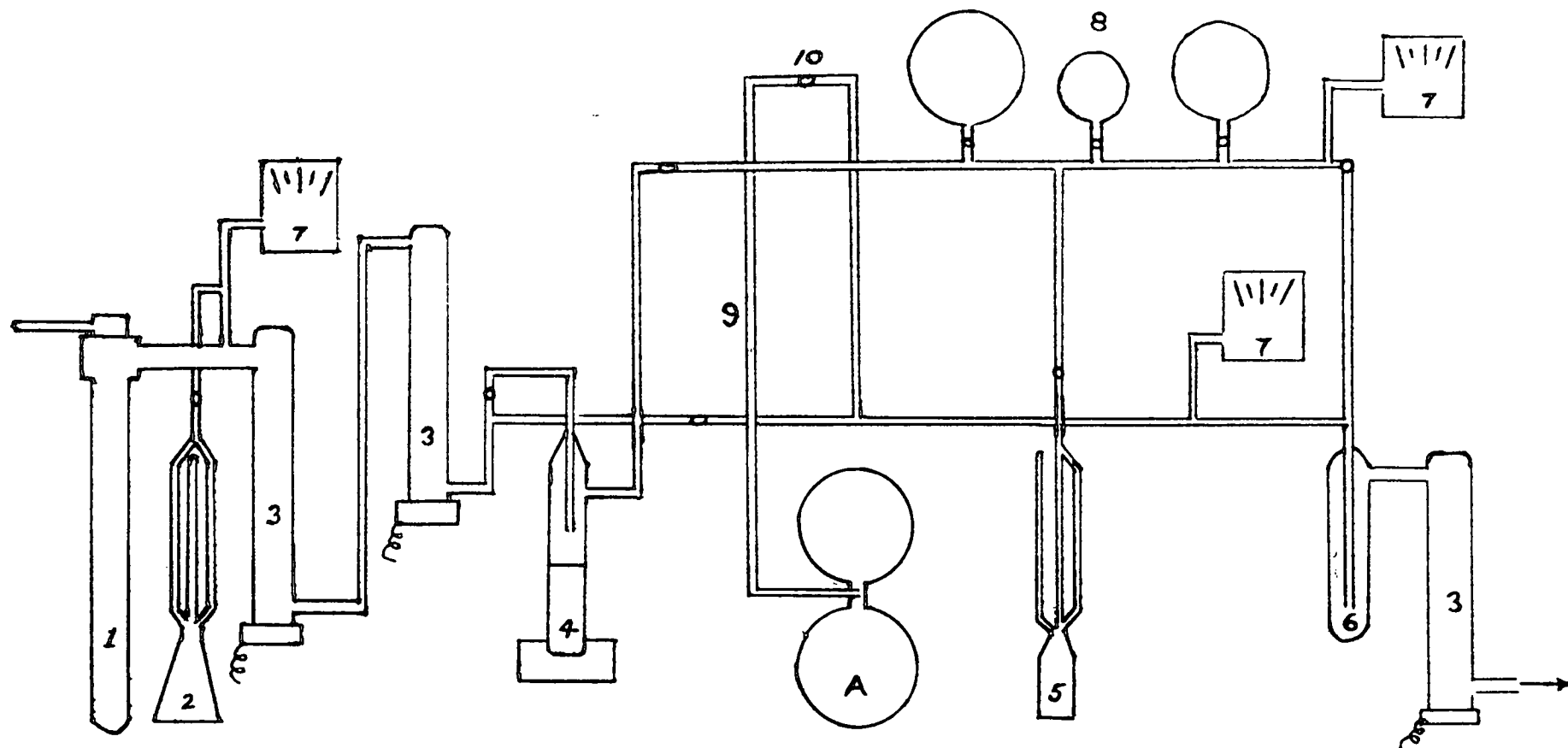
An aliquot of the gas from a sample is taken into a special analyzer (Figure 3). The gas is confined in the copper oxide tube by raising the mercury in the analyzer bulb. Hydrogen is removed as H₂O with anhydrous and carbon dioxide is removed with Ascarite. Pressure differentials are read on the "leg" of the analyzer which serves as a manometer during analysis. The results of this analysis are calculated to standard conditions and to weight per cent of the gases in the sample after correcting for the blank. A similar type analyzer is described in the literature (5).

NOTES

1. The apparatus can, of course, be employed to determine gases in other materials, i.e., tantalum, titanium, tungsten, iron and steel, etc. Flux, temperature, time, etc. will necessarily have to be varied to suit each specific analysis.
2. Crucible - 7/8 x 3-1/2 inch - CCH Grade (National Carbon Company)
Funnel - 1-1/2 x 1-3/16 inch - CCH Grade
3. Sample Preparation - Solid samples are cut into 1/4-inch cubes and cleaned with 70% HNO₃-30% HF solution or abraded with a file, washed with benzene or acetone, and air-dried. Finely divided samples are weighed into tin capsules (5 mm. by 13 mm.). All samples are wrapped with approximately twice their weight of 0.001 inch platinum sheet.

REFERENCES

1. Report of Oxygen Sub-group Niobium Task Force, Division M, Committee E-3, A.S.T.M., Atlantic City, New Jersey, June 23, 1959 (revised August 1959)
2. Guldner, W. G., Talanta, 8, 191-202 (1961)
3. Yeaton, R. A., Vacuum, 2, No. 2, 115-124 (1952)
4. "The Determination of Gases in Metals," Special Report 68, Iron and Steel Institute, London, England (1960)
5. Saunders, K. W., Taylor, H. A., Journal of Chemical Physics, 9, 616-625 (1941)



- | | |
|--------------------------------|-------------------------|
| 1. Furnace (Figure 2) | 6. Liquid nitrogen trap |
| 2. McLeod Gauge | 7. Piranni Gauges |
| 3. Diffusion pumps | 8. Calibrated volumes |
| 4. Toepler pump | 9. Manometer |
| 5. Todd Universal Vacuum Gauge | 10. Aliquoting stopcock |
- A. Analyzer (Figure 3)

Figure 1 - Constant Volume "Micro" Vacuum Fusion Apparatus

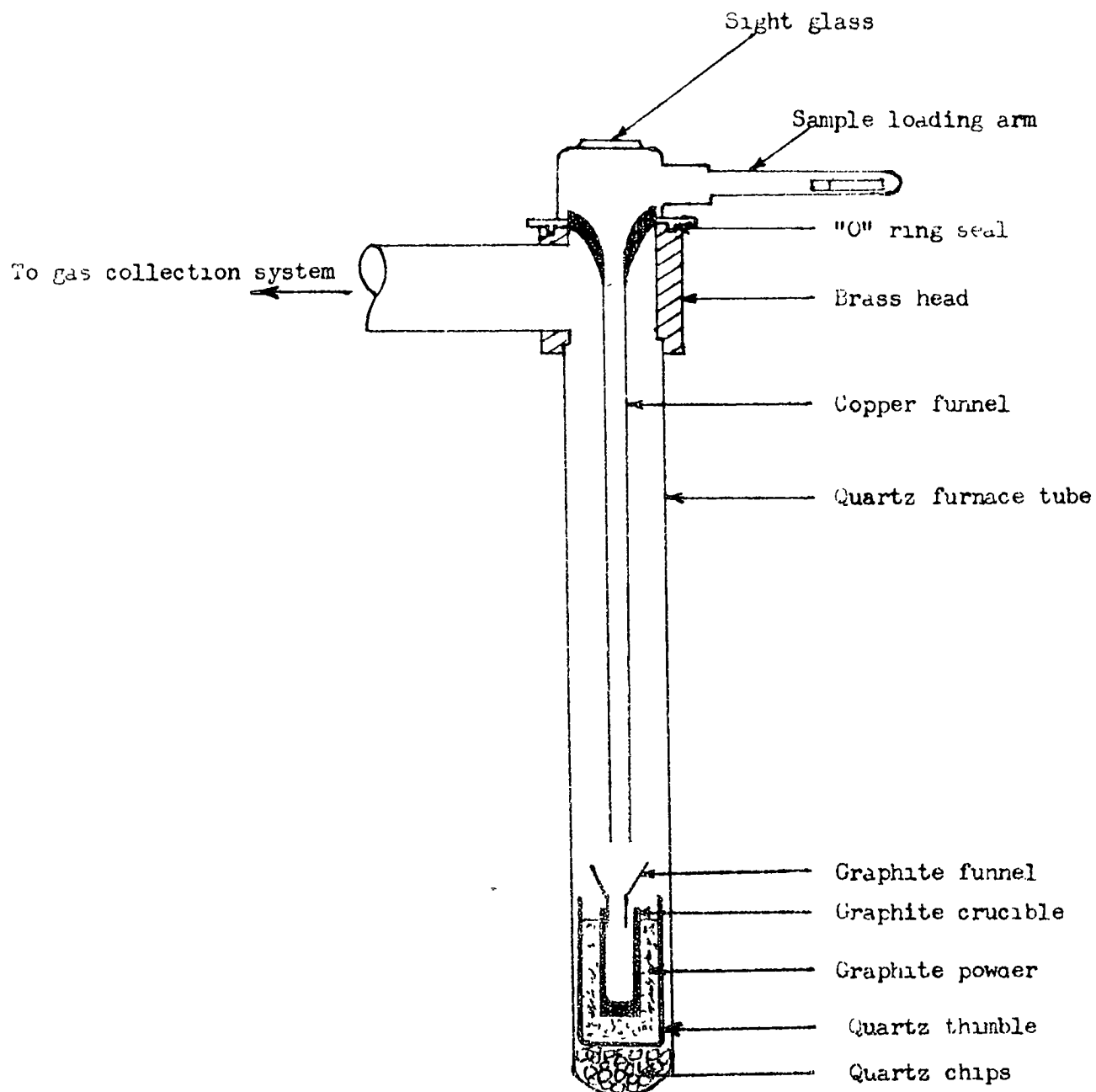


Figure 2 - Furnace Assembly

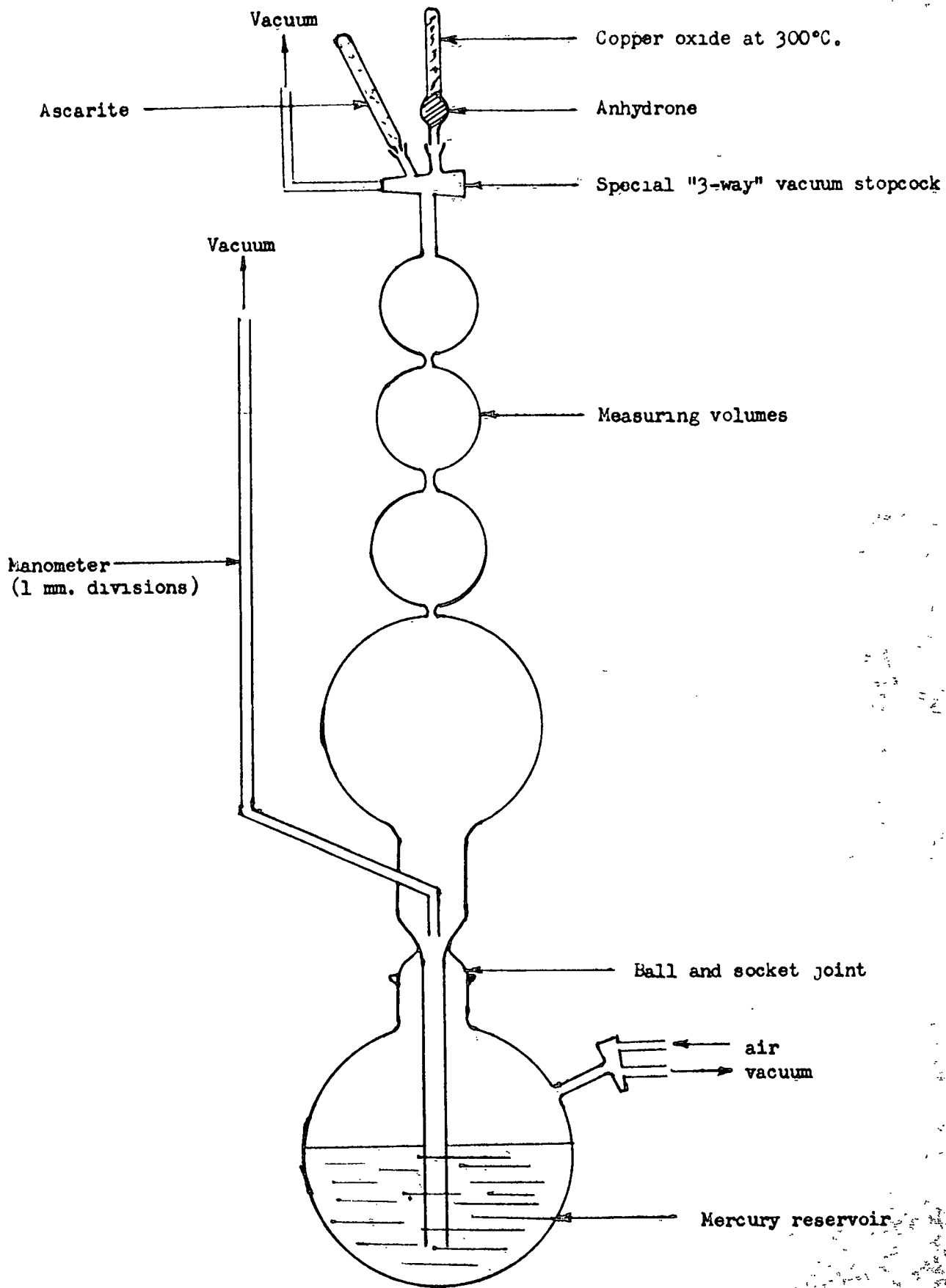


Figure 3 - Gas Analyzer